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Studies in Metallosupramolecular Chemistry

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by

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Acknowledgments

If someone had asked me what I wanted to do with my life, during my undergraduate years here at Canterbury, I never in a million years would have thought I would end up completing a PhD in Chemistry. But here I am older, and somewhat wiser, about to begin the next stage of my life. The journey over the last four years has been a bit like a rollercoaster ride full of both good and bad times in science and life. Of course this journey and this thesis would not have been possible without the help and support of numerous people around me, therefore I would like to take a moment to acknowledge some of these people.

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Abstract

Metallosupramolecular chemistry involves the construction of nanoscale molecular assemblies by reacting metal atoms with bridging organic ligands. The metal atoms act as a type of molecular 'glue' binding together the organic ligands in specific orientations. Thus, appropriate combinations of metal ions and ligands lead to the controlled self-assembly of interesting one-, two- and three-dimensional molecular aggregates.

This thesis details the preparation of a range of novel flexible bridging heterocyclic ligands using conventional organic synthesis, and then explores their reactions with a variety of transition metal precursors. By varying the nature of the organic ligand and the transition metal precursor, new and exciting supramolecular topologies and architectures can be formed. A total of forty-eight ligands were synthesised in this work, forty-seven of which are new compounds. The majority of the ligands synthesised were based around commercially available bisphenol cores. All forty-eight of the ligands had nitrogen heterocyclic groups as coordinating units.

The ligands discussed in this thesis can be divided into three main sections. The first involves the synthesis and coordination chemistry of two-armed ligands based around the Bisphenol A, Bisphenol Z and Bisphenol AP cores. The second section describes the synthesis and coordination chemistry of the larger Bisphenol P and Bisphenol M based two-armed bridging ligands. The third section describes the synthesis and coordination chemistry of various multi-substituted ligands, including tripodal ligands based around a trisphenol core, four-armed ligands and six-armed ligands.

The two-armed bisphenol based ligands proved very successful as synthons in metallosupramolecular chemistry and produced many products with a variety of different metal atoms. The complexes characterised included discrete dimeric products, coordination polymers and a number of helicates, including a dinuclear quadruply-stranded helicate.

Multi-armed ligands are topical, because they have multiple coordination sites that are capable of binding and bridging multiple metal atoms. Such coordination can lead to the construction of cage-like species and complicated networks. A series of three-armed ligands based around a trisphenol core were synthesised with the intention to use these to form such species on coordination with appropriate metal salts. Indeed, one of the products of self-assembly was an interesting M_3L_2 cage. Various other multi-armed ligands were also investigated.

The ligands and complexes in this thesis were characterised by a variety of structural techniques, such as ^{1}H NMR, ^{13}C NMR, mass spectrometry, elemental analysis and X-ray crystallography when crystals were obtained. The crystal structures of twenty-seven ligands and forty-three complexes are described.

Chapter One

Introduction

Chapter One

Introduction

Supramolecular chemistry

Supramolecular chemistry[1] is a relatively new and emerging area of chemistry. Jean-Marie Lehn defined supramolecular chemistry as the "chemistry of molecular assemblies and of the intermolecular bond" and it is sometimes expressed as "chemistry beyond the molecule".[1-3] This definition expresses how in supramolecular chemistry one investigates the way in which different chemical species associate and interact with one another with the generation of a new entity. This has since become one of the most well-known definitions to express and define the term supramolecular chemistry and Jean-Marie Lehn won the Nobel Prize for his contributions in this area of chemistry.[1-3]

Traditionally organic and inorganic chemists have constructed molecules in a step-wise manner from individual atoms and covalent bonds, in which the covalent bonds act as a type of 'glue' in binding the atoms together. Such covalent bonds between the atoms are usually very strong and hard to break. In contrast, supramolecular chemistry involves the use of non-covalent interactions to hold together larger assemblies of molecules, in which multiple intermolecular interactions occur simultaneously to connect the molecules together. These weaker non-covalent interactions consist of such interactions as hydrogen bonding, electrostatic interactions and π-π stacking interactions. Supramolecular synthesis utilises the idea that whole molecules and ions are considered to be the 'building blocks' and the non-covalent interactions are the means of holding or 'gluing' the 'building blocks' together in a self-assembled way. While such intermolecular interactions are weak in comparison to covalent bonds, they still allow for the formation of the most thermodynamically stable species. Since such weaker intermolecular interactions are easily broken and reformed during the course of the reaction, a variety of other intermediate 'kinetic' products are formed along the way. In a sense, during the course of the reaction the building blocks shuffle through many possible products until they get to the most 'attractive' entity or, in chemical terms, the most thermodynamically stable species. This is a type of built in error-checking system between the molecular components.[1, 2, 4]

The concepts behind supramolecular chemistry are not new and there are many examples in nature that use the ideas of self-assembly for biological design. Probably the most famous example of this is DNA, whose biological structure is self-assembled through multiple weak intermolecular interactions, such as hydrogen bonding, π-π stacking and hydrophobic interactions.[1] There are also many other biological examples of supramolecular chemistry in action, such as the polymerisation of actin monomers into filaments, which is important in human cell function.[5]

One of the most common intermolecular interactions in supramolecular chemistry and in nature is hydrogen bonding. Hydrogen bonds occur when a hydrogen atom is attached or bonded to an electronegative atom or electron withdrawing group that draws the hydrogen atom towards a dipole of close proximity. Therefore, in a sense hydrogen bonding is almost like a dipole-dipole interaction.[1, 6] The strengths of such hydrogen bonding interactions are reasonably weak, lying within the range of 5-50 kJ mol^{-1}.[7, 8] There are also a number of other important intermolecular interactions in supramolecular chemistry that are listed below. These interactions are:

(a) Electrostatic interactions (ion-ion, ion-dipole and dipole-dipole);

(b) Van der Waals forces;

(c) Hydrophilic or hydrophobic interactions;

(d) π-π stacking interactions;

(e) Host-guest interactions.

One of the most important and common interactions utilised in supramolecular chemistry is π-π stacking interactions between aromatic molecules.[9] The two types of π-π stacking interactions that can occur between aromatic molecules are illustrated with benzene rings in figure 1.1. The first type of interaction **(a)** is called a face-to-face π interaction, which occurs when the rings are aligned parallel to one another and slightly offset or 'slipped'. Studies have shown that aromatic rings that are arranged directly parallel on top of each other are not as favorable to those that are slightly offset.[10] The second type of interaction **(b)** is known as an edge-to-face interaction.[11, 12] As the name suggests, this interaction occurs between the edge of one ring and the face of the other.

Edge-to-face π interactions are similar to hydrogen bonds. Once again π-π stacking interactions are considered to be reasonably weak, ranging in strength between 0-50 kJ mol^{-1}.[1] Examples of both types of π-π stacking interactions will be discussed in this thesis.

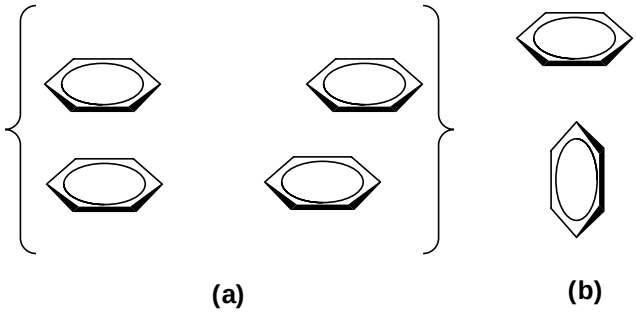


Figure 1.1 – *The two types of π-π stacking interactions that can occur between aromatic rings.* ***(a)*** *Face-to-face and* ***(b)*** *edge-to-face π-π stacking interactions.*

Metallosupramolecular chemistry

Metallosupramolecular chemistry[13, 14] is a subset of supramolecular chemistry involving the self-assembly of metal atoms and ligands (organic molecules) as the building blocks to construct larger assemblies. The coordination bonds that are formed between the ligands and the metal atoms are effectively the supramolecular 'glue' that binds the building blocks together.[15, 16] The strength of the metal-ligand bond varies from very weak to extremely strong depending on the specific nature of the metal atoms and the organic ligands.[17] These coordination bonds between the metal atoms and the ligand molecules are effectively more important than the supramolecular interactions discussed previously, which nevertheless play a significant secondary role in the stabilisation of the final structure.[18] The chemistry involved in the way in which these building blocks interact with one another is an interplay of both thermodynamic and kinetic factors. This interplay shows a dependence on the original properties of the individual components or building blocks. The dependence is shown by the availability of many metal salts, each with different properties, which allows for the use of particular metals for certain applications.

A whole new area of chemistry has opened up for exploration since the addition of metal atoms into supramolecular structures. Furthermore, the simple one-pot self-assembly reaction of the building blocks has resulted in the construction of a large number of fascinating structural topologies such as complex polyhedra, helicates, cages, catenates, rotaxanes and knots.[2, 19, 20] The metal atoms in a metallosupramolecular structure play an important role in the formation of a particular species with organic ligands to give the overall structure particular properties. This is because the metal atoms can adopt specific coordination geometries and act as orientation centres for the formation of a variety of structures. The particular properties that metal atoms can give the final metallosupramolecular assemblies can be photophysical, electrochemical, magnetic and spectroscopic.[2, 19, 20] Consequently many metallosupramolecular structures have been used for practical applications in the real world, such as in the development of molecular devices and machines.[21-23]

Complementary information is encoded into both the organic ligand and metal atoms to allow for the pre-programmed self-assembly of the components into a single structure.[3] For this to occur the metal atom must have a certain degree of lability for the formation of the desired thermodynamic product over other kinetic products. Another pre-programmed feature encoded into the metal atom is its preferred geometry. These two aspects are important pieces of information to take into consideration when choosing a metal atom for a metallosupramolecular assembly.

The metals chosen in metallosupramolecular assemblies usually have preferred coordination numbers and geometries. An outline of the most common metal atom coordination geometries is shown in figure 1.2.

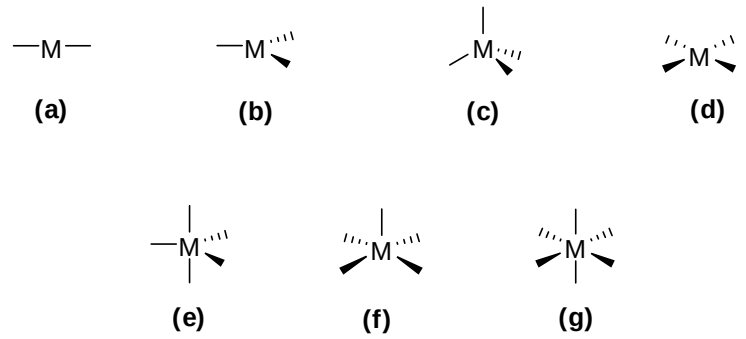


Figure 1.2 - *A schematic of the coordination geometries of metal atoms used in metallosupramolecular chemistry.*

The monovalent d^{10} metals silver(I) and copper(I) have no strong preference for particular coordination numbers or geometries and have been shown to form a vast array of interesting metallosupramolecular assemblies.[24-26] Silver(I) often coordinates to ligands with lower coordination geometries in order to maximise the space between ligands. These lower coordination geometries can be two-coordinate, as illustrated in **(a)**, or trigonal **(b)** or T-shaped three-coordinate. On the other hand copper(I) shows a preference for a four-coordinate tetrahedral geometry, as illustrated in **(c)**. As a consequence of the lability of these d^{10} metal ions, both have been used extensively throughout the course of this research. However, other metal atoms that prefer specific coordination numbers and geometries have also been employed. An example is copper(II). The copper(II) d^9-metal can adopt a variety of coordination modes from four-coordinate tetrahedral through to six-coordinate octahedral, as illustrated in **(c)** through to **(g)**, often preferring the five-coordinate geometries trigonal bipyramidal **(e)** and square pyramidal **(f)**. Another example of a metal atom with a particular preference for a specific coordination geometry is the d^8-metal palladium(II). Palladium(II) prefers the four-coordinate square-planar geometry, illustrated in **(d)**. A number of other metals were used to generate metallosupramolecular assemblies in this thesis, such as cobalt(II), cadmium(II), nickel(II) and zinc(II). Cobalt(II) and zinc(II) can just as easily adopt a six-coordinate octahedral geometry, as illustrated in **(g)**, or a four-coordinate tetrahedral geometry **(c)**. Cadmium(II) prefers an octahedral coordination geometry or higher coordination number than those shown in figure 1.2.

Another factor to take into account when choosing the appropriate metal salt is that of the associated or coordinating anions. Such anions can have an important effect on the coordination mode of the complex by playing a vital role in the overall structure, often occupying coordination sites on the metal atom itself. Some examples of coordinating anions are nitrates, halides and acetates, just to name a few. There is a certain degree of unpredictability with the mode of coordination of such anions in metallosupramolecular structures and as a consequence one cannot predict where and how many coordination sites will be occupied by such anions. Some coordinating anions are capable of bridging or chelating to the metal atoms. A well-known example of a metal salt that can bridge together metal atoms is copper(I) iodide. Such bridging copper(I) iodide motifs are not uncommon and there have been many examples in the literature of iodine bridging copper(I) atoms in a variety of different ways from simple Cu_2I_2 square motifs to much

more complicated copper(I) iodide clusters.[27] Another way to overcome the unpredictability of coordinating anions and regain some control over the coordination sites of the metal atom is to bind a strong chelating ancillary group to the metal center before the self-assembly reaction takes place. An example of such an ancillary group is ethylenediamine bound to a palladium metal centre.[28] Some anions are non-coordinating and consequently have little effect on the overall metallosupramolecular structure. Examples of two non-coordinating anions are hexafluorophosphate and tetrafluoroborate. If no anion or anions occupy any of the coordination sites on the metal atom there are more coordination sites available for interactions between the metal center and the organic ligand. There can be difficulties incurred when crystallising complexes using metal atoms and non-coordinating anions, because such anions will somehow need to be incorporated into the crystal lattice. As a result of this the non-coordinating anions can often be disordered.

Another important factor to take into account when constructing metallosupramolecular assemblies and arrays is the bridging organic ligand. The ligand can have as much influence on the overall final structure as the metal atom. Essentially bridging ligands are a lot more complex than single metal atoms, due to their unlimited size and structural complexity. Ligands can have multiple donor atom sites and various bridging capabilities, which therefore increases the potential complexity of the final structure. One must also use ligands with donor atoms that allow the formation of labile metal-ligand coordination bonds in order to maintain the thermodynamic control. In this context a vast amount of supramolecular chemistry has been carried using nitrogen containing heterocyclic ligands, which were used in this research and will be discussed in more detail in the next section.

Nitrogen-containing heterocyclic ligands

Nitrogen-containing heterocyclic ligands have been used extensively in ligand design in the field of coordination chemistry.[29] There are two quite different groups of nitrogen-containing heterocycles, which are based around the size of the aromatic ring. The two groups are the ‘azines’, which are the six-membered aromatic rings, and the ‘azoles’, which are the five-membered aromatic rings. The azines are π-deficient six-membered

aromatic rings, which form metal complexes by coordination through the nitrogen atom. The simplest example of a π-deficient aromatic azines group is pyridine, as shown in figure 1.3**(a)**. Another simple example of an azine group is quinoline. Both of these azine groups have been used extensively throughout this thesis. On the other hand, the azoles, which are five-membered aromatic rings, are π-excessive. One of the most well-known examples of a π-excessive azole is pyrazole, as depicted in figure 1.3**(b)**. The NH group of the pyrazole donor group can also be deprotonated to form an anionic pyrazolate than can coordinate to metal atoms.[30-32]

(a) **(b)**

Figure 1.3 – *Examples of an azole and an azine nitrogen-containing heterocyclic ring used in coordination chemistry.* ***(a)*** *pyridine and* ***(b)*** *pyrazole.*

The two simple nitrogen-containing heterocyclic ligands mentioned above are often incorporated as donor subunits of much larger molecules. The larger molecules within which the heterocycles are appended can be structurally diverse and ligands with two or more binding domains are common in metallosupramolecular chemistry. The Steel group often designs ligands that consist of two or more nitrogen-containing heterocycles attached to a central arene core by a spacer group containing one or more atoms.[29]

Some of the simplest ligands that have been used as synthons in metallosupramolecular chemistry are bridging ligands containing two binding domains. Some examples of bridging ligands that can coordinate to two metal atoms are shown in figure 1.4.

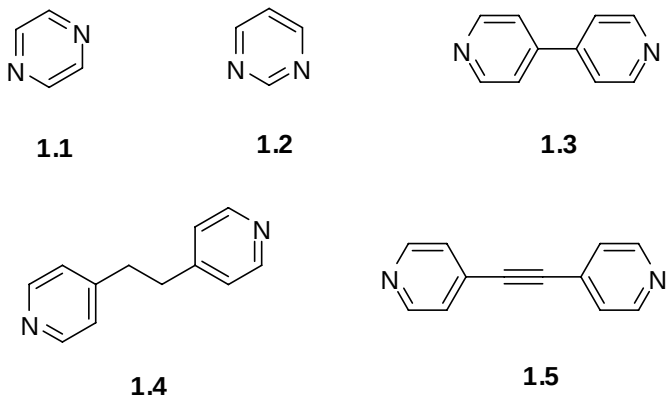


Figure 1.4 - *Some examples of bridging ligands that can coordinate to two metal atoms.*

Pyrazine, **1.1**, is one the most well-studied bridging ligands in metallosupramolecular chemistry.[29, 33] It has been used extensively as a bridging ligand by itself, as in the Creutz-Taube mixed valence ion, or as part of a larger ligand molecule. The distance between the metal atoms in complexes bridged by pyrazine is approximately 7Å.[29, 33] Pyrimidine, **1.2**, is another simple example of a bridging azine ligand that has been employed as a ligand itself and as part of a larger molecule. As expected the distance between the metal atoms in complexes bridged by **1.2** is shorter than that of pyrazine, being approximately 6Å.[33] The distance between metal atoms in complexes is important, because if one has control over the distance between metal atoms one can therefore synthesise complexes with specific dimensions. There has been a lot of study on the design and construction of bridging ligands with varying distances between nitrogen donor atoms. Ligands **1.3-1.5** are some examples of such ligands that have been used as synthons in metallosupramolecular chemistry. The rigid 4,4'-bipyridine ligand **1.3** has been well studied, forming many supramolecular arrays with a metal-metal distance in complexes of approximately 11Å.[29, 33] The metal-metal distances can also be increased further by addition of various spacer groups between the nitrogen heterocyclic rings, as illustrated by ligands **1.4** and **1.5**. The spacer group can either be rigid as in ligand **1.5** or flexible as in ligand **1.4**.

Ligand Design

The overall design of the bridging ligand is very important for the construction of specific metallosupramolecular assemblies. There are essentially three parts within a ligand, each of which can be modified and altered to achieve desired properties. The first part of the ligand is the central core unit, which can be anything from a single carbon atom to an aromatic benzene ring. The second components are the spacer groups, which link the donor groups to the central core unit. The third component is the donor group, which in this research are nitrogen-containing heterocycles. Of course, one is not limited to what has been mentioned above and there are numerous central cores, spacer groups and donor groups that can be employed. The Steel group has spent many years successfully designing and synthesising ligands that contain nitrogen-containing heterocyclic groups attached to a central arene core by various flexible spacer groups. Subsequently, many complexes with interesting supramolecular topologies have been generated.

The choice of spacer groups is very important in ligand design, because the overall flexibility and size of the ligand is controlled by the spacer group. Such spacer groups can be rigid or flexible in nature. The advantages of a rigid ligand over a more flexible ligand relate to the rational design of simple products, such as symmetrical polygons, due to the predictability of the combination of the ligand and metal atom geometries. In contrast flexible spacer groups, such as alkyl chains, can lead to the formation of less symmetrical assemblies, due to the inherent flexibility of the spacer groups. Flexible ligands are also more prone to chelate to single metal atoms. In short, flexible ligands can form more fascinating structural topologies than their rigid ligand counterparts and therefore the focus in this thesis is on new flexible ligands.

Complex design

Metallosupramolecular chemistry involves the construction of nanoscale molecular species by reacting metal atoms with ligands, in which the metal atoms effectively act as a type of supramolecular ‘glue’ binding together the ligands in specific orientations. There are numerous assemblies that one can form using this methodology, from simple discrete species and polymers to more intricate three-dimensional species such as cages.

A simple example of this type of methodology is a molecular square. First reported in the early 1990's, by Fujita and co-workers, a molecular square geometry requires the self-assembly of four rigid sides bound together by four appropriate 90° corner units. Fujita and co-workers reported such a molecular square architecture upon mixing combinations of the metal-containing reactants with the nitrogen heterocyclic ligand 4,4'-bipyridine in ethanol-methanol-water,[34, 35] as depicted in figure 1.5. A molecular square contains a central cavity, which has potential use in areas like catalysis, separation technology and sensors.[15, 36] Therefore there has been interest in the extension of this approach to polyhedra with internal cavities, especially three-dimensional cubes and cage-like assemblies.

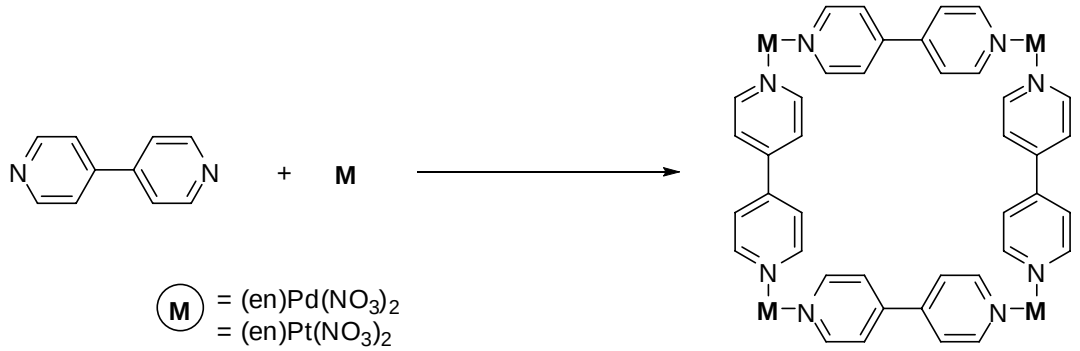


Figure 1.5 – *Illustration of the molecular components required for the self-assembly of a molecular square designed by Fujita and co-workers.*

The molecular square designed by Fujita and co-workers has the organic ligands forming the linear bridging components of the square and the metal atoms as the angular corner components. However, one is not limited to this design strategy and there are other ways to construct a simple square polygon, in which the ligand acts as the 90° angular component and the metal atom is the linear component. An example of this is the molecular square reported by Sharma et al., shown in figure 1.6, which has pyrimidine bridging ligands as the angular components and silver atoms as the linear components.[37]

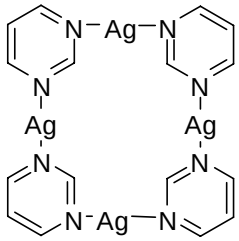


Figure 1.6 – *Example of a molecular square with pyrimidine bridging ligands and silver atoms.*

In supramolecular chemistry discrete products, such as the polygons described above, are often thermodynamically more favoured than polymers, which tend to be the kinetic products. Indeed, there has been a vast number of polygons synthesised of various sizes and shapes,[15, 38, 39] some of which contain a large central cavity which encapsulates a guest molecule. As one can imagine there are numerous applications and potential applications for such assemblies, such as catalysis and electrochemical sensing.[15, 38, 39]

The one-pot self-assembly methodology employed by metallosupramolecular chemists has resulted in the construction of a large number of fascinating topologies, such as helicates, molecular cages, catenates and rotaxanes. A helicate can be made by the wrapping of ligand strands around two or more metal atoms about a helical axis. Helicates[40-43] are currently a hot topic in coordination chemistry and will be discussed later in this thesis. Molecular cages are also highly topical due to their potential host-guest applications. Some cages have been shown to facilitate reactions inside the cage between encapsulated guest molecules. Molecular cages will also be discussed further in this thesis with examples from this work. Two other interesting types of complexes in metallosupramolecular chemistry are catananes and rotaxanes.[1, 19] Catananes are compounds that are comprised of at least two rings that are mechanically interlocked. As a result, the rings cannot be parted without the breaking of a chemical bond. A well-known topological example of a catanane is the Olympic rings, shown in figure 1.7. On the other hand rotaxane compounds are composed of one or more macrocyclic rings that have a linear rod-like molecule threaded through the middle. Once again the components once formed cannot be parted without breaking a chemical bond and bulky groups are often placed in the ends of the linear molecule to stop the rings from slipping off.

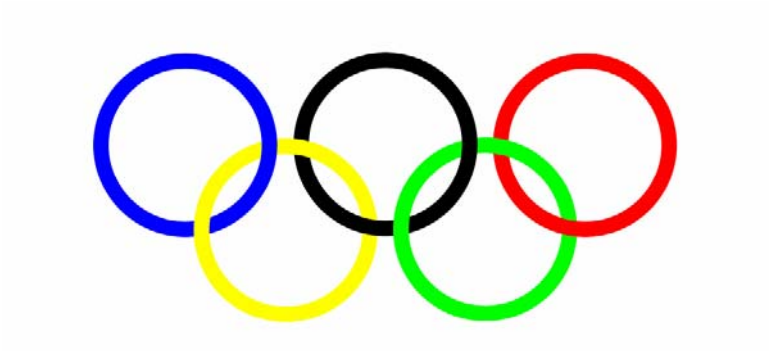


Figure 1.7 – *The Olympic rings.*

Thesis coverage

This thesis describes the synthesis of forty-eight bridging ligands, only one of which has previously been reported. All forty-eight of the ligands synthesised contain nitrogen heterocyclic rings. The X-ray crystal structures of twenty-seven of these ligands were obtained to determine their conformations in the solid state. It is advantageous to measure the distances between the terminal nitrogen donors of these ligands in the solid state, because this will determine the metal-metal separations within their metal complexes. Subsequently, all of these ligands were reacted with a variety of metal salts in the hope of constructing new and interesting metallosupramolecular assemblies. This was successful and over 200 metal complexes were prepared with these ligands in this study. Forty-three of these metal complexes were unambiguously characterised by X-ray crystallography.

All the ligands and complexes described in this thesis were characterised by a variety of techniques such as NMR, mass spectrometry, elemental analysis, melting point and X-ray crystallography, when crystals were obtained.

Chapter two describes the synthesis and coordination chemistry of a range of new two-armed flexible bridging ligands derived from the commercially available precursors Bisphenol A and Bisphenol Z. In total fourteen new bridging ligands were synthesised with various nitrogen heterocyclic groups appended to the Bisphenol cores. The ligands proved to be very successful as synthons for metallosupramolecular assemblies generating a variety of supramolecular structures, many of which were able to be crystallised and fully characterised.

Chapter three describes the synthesis of a series of less symmetrical two-armed ligands based around a Bisphenol AP core, three of which were characterised by X-ray crystallography. Numerous complexes were prepared with the Bisphenol AP ligands, however few were able to be crystallised.

Chapter four focuses on the synthesis of various multi-armed ligands. Currently there is a lot of interest in such ligands for constructing complex cage-like species or complicated supramolecular networks. The first section of chapter four discusses the synthesis and coordination chemistry of three-armed ligands based around a 1,1,1-tris(4-hydroxphenyl)ethane based core. The second section of chapter four concentrates on the synthesis of tetra-substituted ligands, in particular those based around a 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol core. The last part of chapter four focuses on hexasubstituted ligands designed around a dipentaerythritol core.

Chapter five describes the synthesis and coordination chemistry of another two series of flexible two-armed bridging ligands based around the Bisphenol P and Bisphenol M cores. These bisphenol ligands are even more flexible than the Bisphenol A and Bisphenol Z bridging ligands by incorporation of an additional spacer unit within the ligand structure. Once again many complexes were prepared with these ligands, some of which were subsequently crystallised and analysed by X-ray crystallography.

Chapter Two

Bisphenol A and Bisphenol Z based ligands

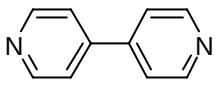
Chapter Two

Bisphenol A and Bisphenol Z based ligands

Introduction

One of the most appealing features of metallosupramolecular chemistry[1, 13, 14, 29] is that it is possible to judiciously construct relatively complex molecular architectures utilising the concept of self-assembly. Complementary structural information is encoded into each of the starting materials that leads to the desired assembly.[15, 16] Thus appropriate combinations of metal ions and ligands can lead to 0-, 1-, 2- and 3-dimensional assemblies, which can possess properties not displayed by the constituent components. This type of methodology has resulted in a number of fascinating structural topologies from simple molecular rods, wires, squares and ladders to more complex molecular cubes, coordination polymers, helicates, interlocked rings (catenanes and knots) and cages.[5, 14, 29, 44-47]

A great deal of study and interest in the area of supramolecular chemistry has focused on the use of 'rigid' ligands as the ideal building blocks for the rational formation of simple symmetrical polygons, such as squares and hexagons, to the more ambitious polyhedra, such as cubes and dodecahedra. Extensive research has shown that these 'rigid' ligands can generate an unlimited number of fascinating structures with unique properties such as magnetic or optical properties and enclathration abilities. 4,4'-Bipyridine (ligand **2.1**), as shown in figure 2.1, is a very well known example of a 'rigid' ligand that has been widely exploited to design and construct hundreds of interesting supramolecular topologies.[48-53]



2.1

Figure 2.1 - *4,4'-Bipyridine*

In contrast, less emphasis has been placed on organic ligands of a flexible nature. Flexible ligands can act as better building blocks in the construction of supramolecular

species and lead to a number of different and fascinating structural topologies that the rigid ligand counterparts cannot achieve. Flexible ligands allow the formation of less symmetrical topologies, such as cages, rectangles and intriguing helicates. For this reason the Steel group has been studying such flexible ligands for some time. The ligands are made more flexible by the introduction of spacer groups, usually constructed from combinations of methylene groups with sulfur or oxygen atoms. The flexibility of such ligands is dependent on the number and type of flexible groups used and the topology of the complex architectures is dependent on the conformation of the organic ligand.

In general, the majority of flexible ligands are assembled from nitrogen containing heterocycles, which are linked by flexible groups. Figure 2.2 illustrates some examples of the simplest nitrogen containing flexible ligands, in which 4-pyridyl groups are linked via a varying number of methylene spacer groups.

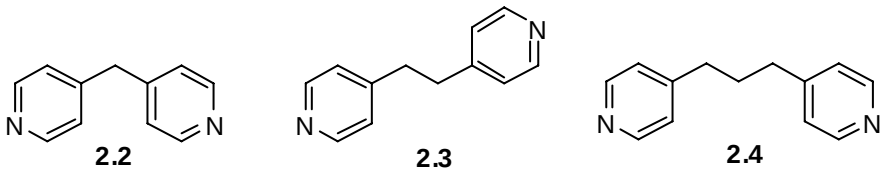
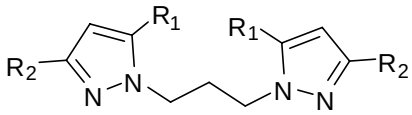


Figure 2.2 – *Some simple examples of nitrogen containing flexible ligands linked by methylene spacer groups.*

Ligand **2.2**, in which the spacer group is a methylene group, forms a two-dimensional network structure with cadmium nitrate.[54] This two-dimensional structure is essentially identical to the two-dimensional grid-like topology prepared from 'rigid' ligand 4,4'-bipyridine and cadmium nitrate. Interestingly, if the methylene spacer group in ligand **2.2** is changed from a sp^3 carbon as depicted to an sp^2 carbon, a one-dimensional coordination polymer made up of dinuclear macrocyclic units forms.[54] The flexibility of ligand **2.2** can be further enhanced by addition of another methylene group as illustrated by ligand **2.3**. The addition of an extra sp^3 carbon allows the formation of interesting one-dimensional coordination polymers and chains[54-58], one-dimensional arrays,[59-63] through to fascinating three-dimensional networks.[64-72] Several of the three-dimensional networks display particularly interesting topologies; reacting ligand **2.3** with CuSCN results in the formation of two interpenetrating three-dimensional nets displaying a rare

$4^2 6^3 8$ topology.[67] Further extension of the alkyl chain to a propylene group, as in ligand **2.4**, allows the formation of unusual topologies, such as rare one-dimensional polymeric double helices,[73, 74] chains[75] and one-dimensional ribbons of rings entwined with two-dimensional sheets resulting in the self-assembly of a polycatenated three-dimensional architecture.[76] Ligand **2.4** also forms various kinds of two-dimensional networks,[60, 77-90] intricate three-dimensional supramolecular arrays[86, 91-95] and novel supramolecular architectures, such as a complex with an interlaced triple-stranded molecular braid-like topology that looks similar to a hair braid.[96] Subsequently, addition of more methylene spacer groups generating longer alkyl chains allows the creation of not only one-dimensional polymers[60] but more complex two-dimensional nets and three-dimensional arrays.[77, 78, 97]

Most of the research in the field to date has investigated flexible ligands that are constructed from the well known pyridine heterocyclic subunit. Recently, a variety of flexible ligands have also been constructed with other nitrogen containing heterocycles, such as pyrazoles. Figure 2.3 illustrates examples of such ligands containing pyrazole heterocyclic groups that are separated by a flexible propylene spacer unit. Schuitema et al. reported the first complexes of ligands **a-c** with divalent copper, cobalt and zinc, and showed that all the ligands formed almost identical eight-membered chelate rings with each of the metals ions.[98] Following on from this the Steel group studied ligand **a**, 1,3-bis(pyrazol-1-yl)propane, in far greater detail by investigating the self-assembly of ligand **a** with various d^{10} metals like silver, zinc and cadmium.[99] 1,3-Bis(pyrazol-1-yl)propane was reacted with zinc acetate and cadmium nitrate to generate similar mononuclear eight-membered chelete rings to that of Schuitema and co-workers. Intriguingly, reaction of 1,3-bis(pyrazol-1-yl)propane with silver nitrate in methanol generated two different types of metallosupramolecualar species coexisting within the same crystal. One of the species was a discrete M_2L_2 macrocycle, which was stacked in between the two-dimensional network of the second polymeric species assembled from one-dimensional polymeric chains. The one-dimensional chains have weak interactions between silver atoms and the two nitrate oxygens of an adjacent chain resulting in the overall two-dimensional network. In 2003, Flinzner and co-workers reported the self assembly of eight-membered copper chelate rings with ligand 1,3-bis(pyrazol-1-yl)propane and copper(II) tetrafluoroborate.[100]



a) $R_1 = R_2 = H$
b) $R_1 = Me$, $R_2 = H$
c) $R_1 = R_2 = Me$

Figure 2.3 *–Ligands containing pyrazole heterocyclic groups that are separated by a flexible propylene spacer unit.*

Over the last few years, the Steel group has been interested in exploring the topological possibilities of various complexes by use of heterocyclic rings linked to aromatic groups via flexible spacer groups. A generalised picture of such a ligand is shown in figure 2.4. These ligands consist of nitrogen-containing heterocycles attached to a central arene core by flexible spacer groups (X). Of interest to the Steel group is the flexibility to modify all or some parts of the general structure in figure 2.4, in order to achieve the desired properties of ligands. The flexibility of the ligand can be controlled by varying the spacer group (X) by simply changing the type of hetero-atom and or length of the spacer. The heterocyclic group can be substituted for a variety of different groups, such as pyridine, pyrazole and more recently quinoline. Finally, the number of heterocyclic groups (n) attached to the central arene core has been varied, with the number of appended groups dependent on the size of the central arene core.

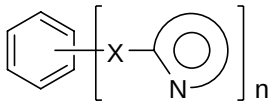


Figure 2.4 *– A stylised representation of flexible ligands that have been made in the Steel group.*

The central arene core, which is represented by the benzene ring in the schematic, is not just limited to a single benzene ring. A large number of aromatic ring systems, including benzene have been investigated by various members of the Steel group, such as naphthalene, anthracene, biphenyls and radialenes.

Previous members of the Steel group have synthesised various flexible ligands based on the generalised structure in figure 2.4, using benzene as the aromatic group, oxygen as the spacer group and pyridine as the nitrogen containing heterocyclic group. Shown in

figure 2.5 are some examples of such ligands that have been designed by various members of the Steel group. Many fascinating 1-, 2-, and 3-dimensional complex structures with interesting topologies have been synthesised from these ligands over the last 10 years. Hartshorn et al. synthesised several ligands based on a para-substituted benzene ring forming a variety of complexes. For example, a M_2L_2 macrocycle was made by reaction of 1,4-bis(2-pyridyloxy)benzene (ligand **2.5**) with silver nitrate.[101] Hartshorn et al. also extended the ligand molecules by addition of spacer groups containing two atoms, where the only isomeric difference between the molecules is the order of the atoms in the spacer groups. Ligands **2.6** and **2.7** formed one-dimensional polymeric complexes with silver nitrate, and a M_2L_2 macrocycle was achieved by reacting 1,4-bis(2-pyridylmethoxy)benzene (ligand **2.7**) with palladium chloride.[102] Subsequently in 1998, McMorran et al. described the self-assembly of the first quadruple helicate generated from ligand **2.8** and a palladium precursor.[103] This intriguing quadruple helicate was found to reversibly encapsulate anion guests, such as perchlorate.

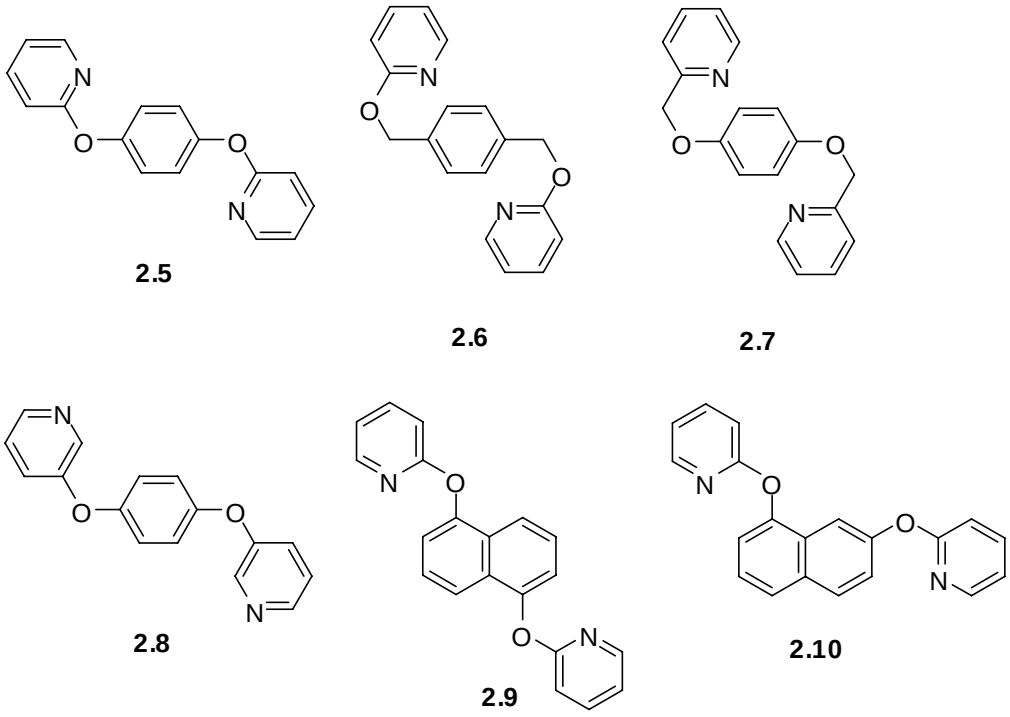


Figure 2.5 - *A few examples of ligands designed by previous members of the Steel group.*

Soon after, O'Keefe et al. synthesised a new series of ligands based around a central naphthalene core in order to investigate the difference it would make by extending the distance between the two silver centers. Two representative examples of these ligands are illustrated by ligands **2.9** and **2.10** in figure 2.5. Ligands **2.9** and **2.10** on reaction with silver nitrate self-assembled into a one-dimensional zigzag polymer and a single stranded helicate, respectively.[104]

In order to investigate even more metallosupramolecular architectures, one can also change the type of heterocyclic group appended to the central benzene core. Previous members of the Steel group have prepared a range of examples of ligands with different heterocycles attached to the benzene core are shown in figure 2.6. Ligand **2.11**, which has 8-hydroxyquinoline attached to the benzene ring, on reaction with silver triflate leads to a compact circular helical architecture made up of three silver atoms bridged by three ligands in a circular array.[105] Fitchett et al. designed and synthesised flexible ligands with pyrazine and quinoxaline heterocycles appended to the central benzene core (ligands **2.12** and **2.13**). Ligands **2.12** and **2.13** were combined with copper(I) iodide to form two-dimensional sheets comprised of the ligands linked to ladders of Cu_2L_2 rings.[106]

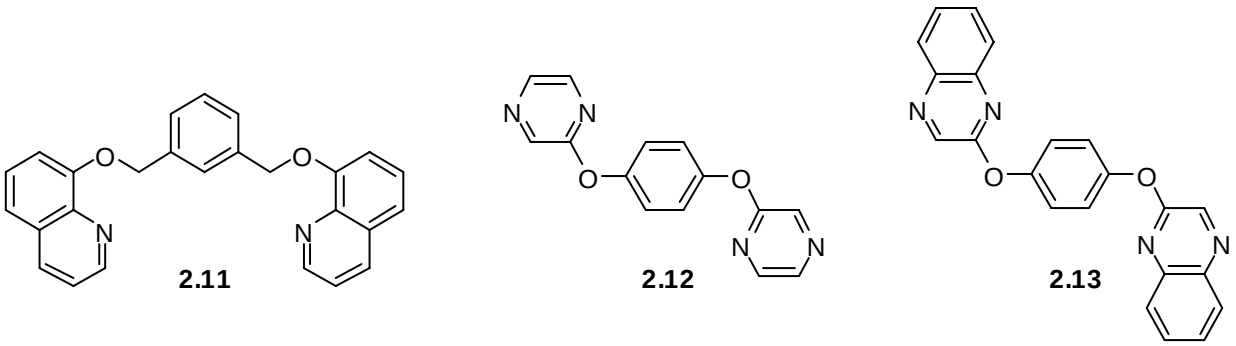


Figure 2.6 – *More examples of ligands designed by the Steel group with various heterocycles attached to a benzene core.*

During his PhD, Fitchett designed a range of flexible ligands that led to the formation of many complexes with novel topologies. The flexible ligands were analogous to Hartshorn's work and were designed around an aromatic benzene core with methylene oxygen spacer groups and pyridine as the nitrogen containing heterocycle. The ligands synthesised were centred on hydroquinone, catechol and resorcinol based cores. The

coordination chemistry of these ligands was investigated and numerous complexes and crystal structures were obtained.[106, 107]

Two armed bridging ligands often lead to complexes bridging only two metal centers resulting in 1-dimensional and 2-dimensional architectures. On the other hand tripodal ligands can bridge up to three metal atoms hereby allowing greater conformational freedom and addition of another level of dimensionality into the structure. With this in mind the Steel group has investigated many multisubstituted heteroaryl ligands over the years. Figure 2.7 shows three flexible tripodal ligands that have been synthesised.

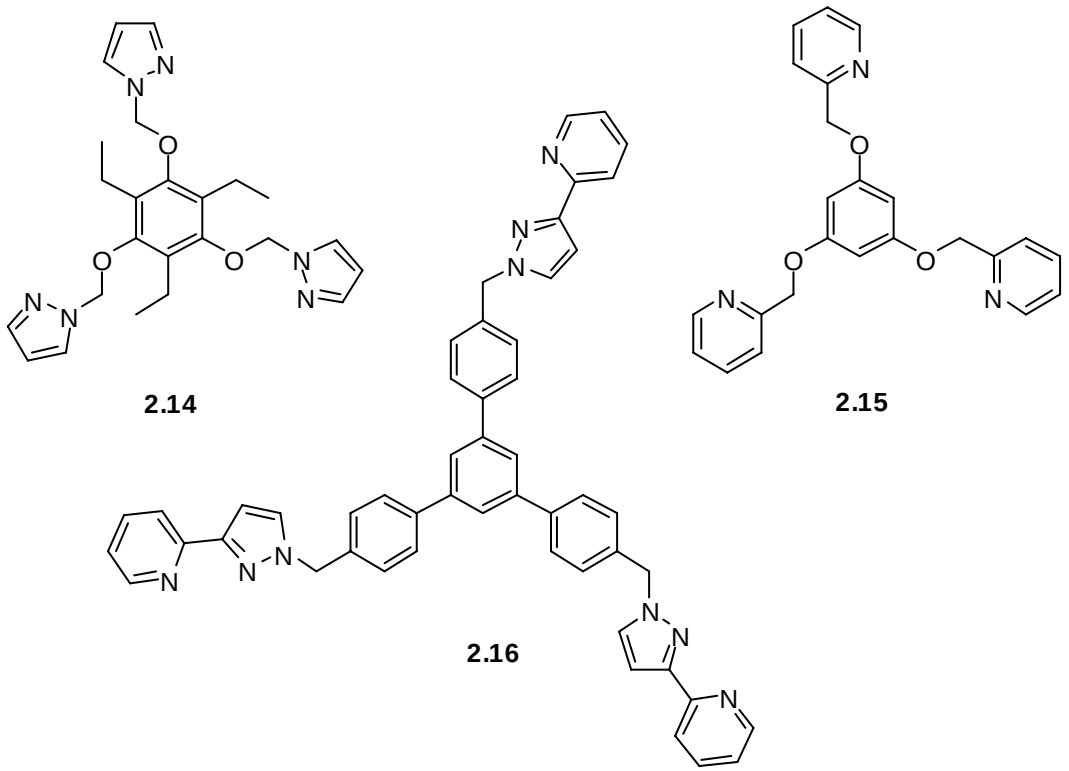


Figure 2.7 – *Examples of flexible tripodal ligands designed by past members of the Steel group.*

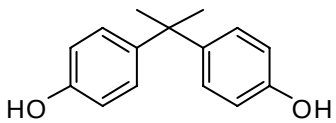
In 1997, Hartshorn et al. described the reaction of ligand **2.14** with $PdCl_2$ resulting in the self-assembly of one of the first examples of a highly symmetric M_6L_4 adamantanoid cage.[108] Nestled within the central core of the cage lies a DMSO molecule, which fits perfectly inside the 4.7Å internal cavity of the cage. Fitchett et al. reacted the tridendate ligand **2.15** with copper(II) chloride to create a structure with a [6,3]- net topology. This structure looks a lot like the structure of a honeycomb, being made up of large M_6L_6 macrocyles.[107] Recently, Zampese et al. made a fascinating

M_6L_4 cage-like structure with the larger tripodal ligand **2.16** and copper sulfate.[109] Each copper sulfate hinges together two ligands and sits on a vertex of the structure. The flexibility of the ligand allows each hinge to twist the structure so as to compress any potential central cavity. The resulting structure is a discrete M_6L_4 cage that has collapsed in upon itself so that it does not contain a central cavity, as the large ligands are aromatically stacked and fill the centre of the structure. New flexible tripodal ligands will be discussed in more detail later on in this thesis.

This chapter will investigate and describe the synthesis and properties of a new range of two armed bridging flexible ligands derived from commercially available Bisphenol A and Bisphenol Z. These bisphenols were reacted with various haloazines and chloromethylpyridines that were chosen based on previous experience in the Steel group with pyridines, pyrazines, quinolines and quinoxalines.[29] The two heterocyclic donor groups on each ligand are equivalent, making the ligands symmetrical. Symmetry in ligands is a very important aspect of bridging ligand design and similar binding groups encourages the self-assembly of a single crystalline product. As described above, the flexibility of these ligands allows the formation of complexes with unique architectures.[29]

Synthesis of the Bisphenol A based -O- spaced ligands

To work towards the aim of constructing and analysing metallosupramolecular species, ligands based on larger aromatic cores with larger distances between nitrogen donors were investigated. These ligands were designed around a Bisphenol A backbone, consisting of a central rigid propane group linked to two aromatic benzene molecules, as illustrated by ligand precursor **2.17** in figure 2.8. This construction has a 'V-type' arrangement, with the two aromatic benzene groups acting as the arms of the 'V' that are linked to the central propane bridging group.

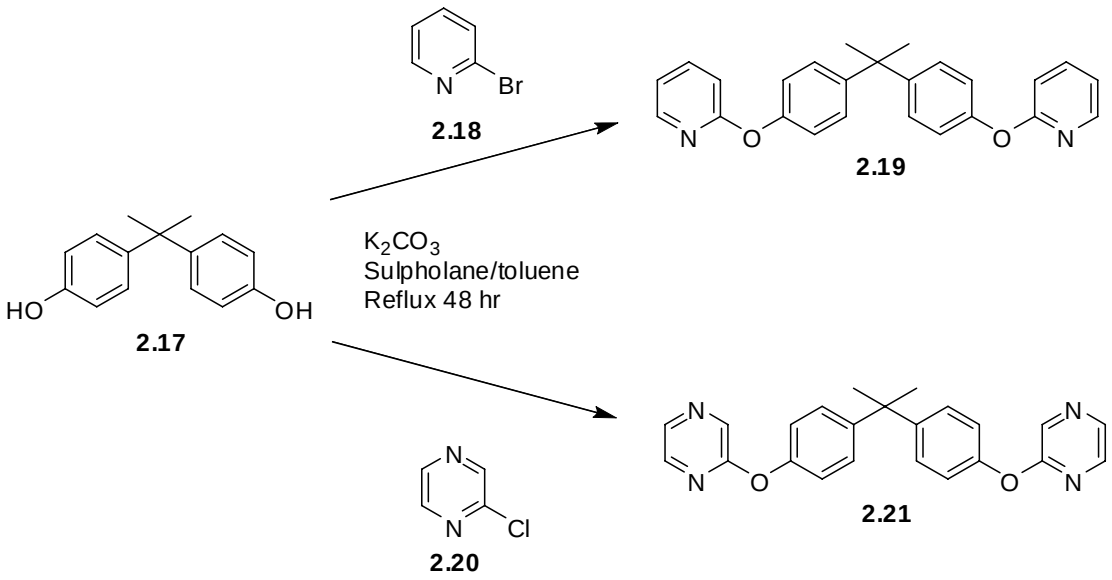


2.17

Figure 2.8 – *Structure of Bisphenol A.*

4,4'-Isopropylidenediphenol, ligand precursor **2.17**, has been in commercial use for many years, being widely known as Bisphenol A and is commercially available at a low price. To date, Bisphenol A has primarily been used in the production of epoxy resins and polycarbonate plastics.[110] These plastics are generally used in a lot of food and drink packaging applications, while the resins are commonly used as lacquers to coat metal products such as bottle tops and food cans.[111] Recently, Bisphenol A has been found to be toxic, especially towards females because of its known hormone disrupting effects.[111] Countless bisphenol derivatives can be manufactured by acid-catalysed condensation of a ketone with two molecules of a phenol.

The first two ligands synthesised from ligand precursor **2.17** are outlined in scheme 2.1. Ligands **2.19** and **2.21** were synthesised in a method analogous to that of O'Keefe et al.,[112] by double nucleophilic aromatic substitution with Bisphenol A. The reaction conditions adopted were to prepare a potassium salt of Bisphenol A in a sulpholane/toluene (2:1) refluxing mixture under an inert atmosphere. Two equivalents of 2-bromopyridine (**2.18**) or 2-chloropyrazine (**2.20**) were then added and the mixture was heated at reflux for 48 hours. Recrystallisation of crude ligands **2.19** and **2.21** from an acetone/water solution gave pure white crystalline solids in 82% and 78% yields, respectively. Subsequently, these ligands were fully characterised by elemental analyses, mass spectrometry, melting points and by ^{1}H and ^{13}C NMR spectroscopy.[113] The ^{1}H NMR spectra of ligands **2.19** and **2.21** were fully assigned by various one- and two-dimensional NMR techniques, such as 1-D TOCSY and GHSQC. Such techniques made it possible to make full assignments of the various aromatic rings by their various integrals and cross couplings. The individual protons of the different heterocyclic groups were also fully assigned by their characteristic chemical shifts and spin-spin couplings. All of these assignments were made easier because of the symmetrical nature of the ligands and comparison of these with structurally related ligands containing these heterocycles from past members of the Steel group.[29] The rest of the ligands throughout this thesis have also been assigned in a similar manner.



Scheme 2.1 – *Synthesis of ligands **2.19** and **2.21**.*

Since one intends to use bridging ligands **2.19** and **2.21** as synthons in the construction of metallosupramolecular assemblies, one is interested in determining their solid state structures. Therefore crystals suitable for single crystal X-ray crystallography were grown. Single crystal X-ray structures of ligands **2.19** and **2.21** were obtained, firstly to confirm their structures and determine their overall conformations in the solid state. Secondly, the distances between terminal nitrogen donors were determined, because this controls the metal-metal separations in metal complexes.

Crystal structure of ligand 2,2-di(4-(2-pyridyloxy)phenyl)propane, 2.19

Colourless block-like crystals of ligand **2.19** suitable for X-ray crystallography were obtained by slow evaporation of an acetone solution. Ligand **2.19** crystallises in the monoclinic space group $P2_1/n$ with a full molecule in the asymmetric unit. The crystal structure of **2.19** is shown in figure 2.9, where the hydrogen atoms are omitted for clarity. Any potential mirror symmetry is lost to ligand **2.19** in the solid state, due to the slight twisting of the benzene rings and the different conformations of the pyridyl ether units. The pyridine rings of the ligand are facing in opposite directions and are considerably tilted away from the mean plane of the benzene rings. This orientation of the pyridine rings away from the mean plane of the phenyl rings is seen more clearly in

the space filling diagram in figure 2.10. The extra flexibility seen on the pyridyl ether units still allows the two nitrogen atoms to point inwards, towards the central cavity between the two benzene rings. The slightly twisted conformation seen in the ligand is reflected in the low N-C-O-C torsional angles of 9.5° and 16.5°. The potential nitrogen donor atoms, which are oriented to face towards each other, have a separation of 8.911Å. Overall ligand **2.19** has a relatively compact structure.

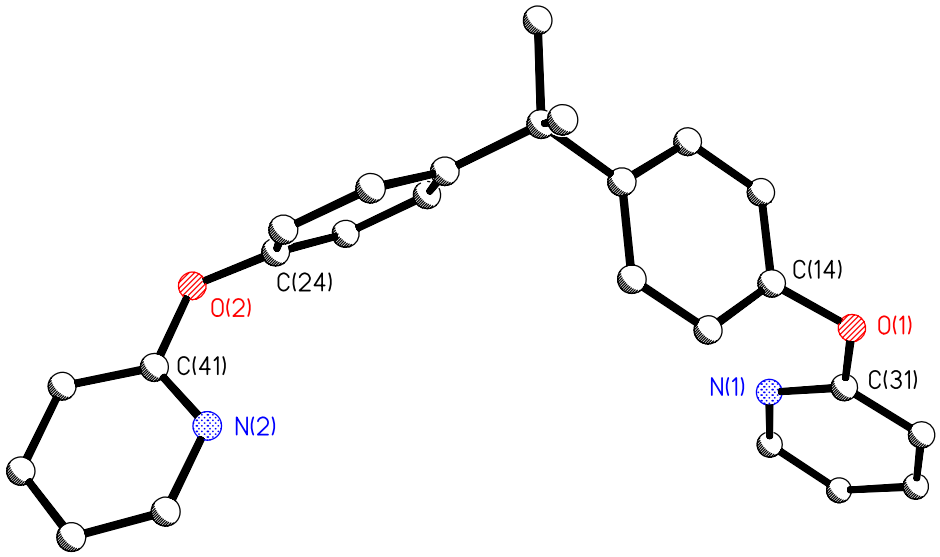


Figure 2.9 – *The crystal structure of ligand **2.19** with hydrogens omitted for clarity. Selected bond lengths (Å) and bond angles (°): C14-O1 1.407(1), O1-C31 1.371(1), C31-N1 1.316(2), C24-O2 1.407(1), O2-C41 1.368(2), C41-N2 1.320(2), C31-O1-C14 119.56(8), N1-C31-O1 119.2(1), C41-O2-C24 118.44(9), N2-C41-O2 119.3(1).*

In aromatic molecules there can be significant π-π stacking interactions between molecules in the solid state. The packing interactions between aromatic molecules can be face-to-face (π-π stacking) or edge-to-face interactions. In the packing structure of **2.19** there are no π-π stacking interactions observed between molecules in the extended structure.

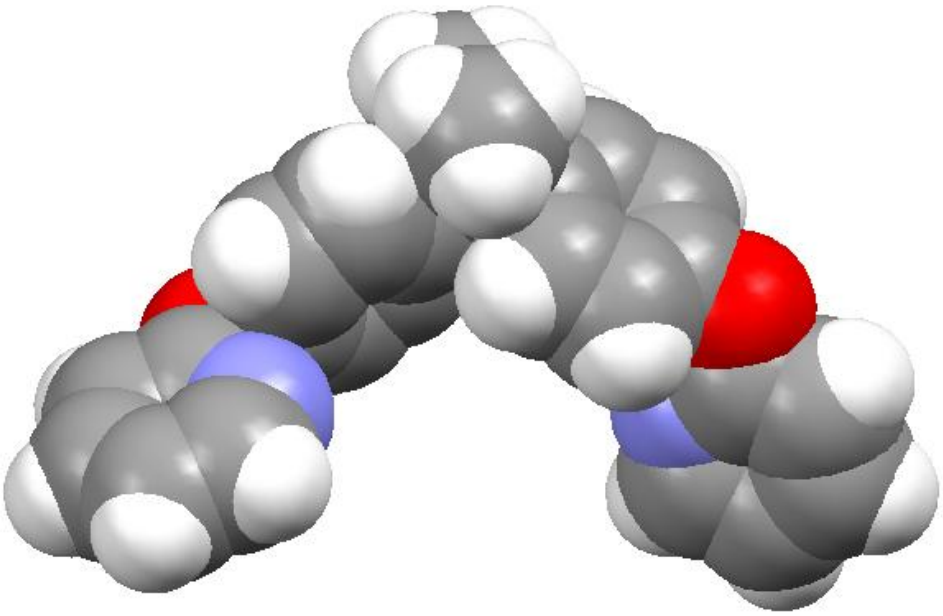


Figure 2.10 – *Space-filling diagram of ligand **2.19**.*

Instead, there is a chain of ligands that runs along the b-axis interacting via C-H···π bonding. The interacting hydrogen atom of the methyl group is found to be 2.622Å away from the mean plane of the neighbouring benzene ring. Ninety degrees away from the first chain is another chain of ligands that is inter-linked in between the first chain by edge-to-face interactions. These edge-to-face interactions are observed between the benzene and pyridine rings (2.782Å) and are considered a reasonably weak interaction.

Crystal structure of ligand 2,2-di(4-(2-pyrazinyloxy)phenyl)propane, 2.21

Good quality pale yellow crystals of ligand **2.21** suitable for X-ray crystallography were also obtained by slow evaporation of an acetone solution of the ligand. This compound crystallises in the monoclinic space group C2/c with half of the molecule in the asymmetric unit. The two halves of the molecule are related by a two-fold rotation axis centred about the quaternary carbon of the propane group. The crystal structure of **2.21** is shown in figure 2.11, where the hydrogen atoms are omitted for clarity. Ligand **2.21** has a more extended shape that stretches outwards more than that of ligand **2.19**. In this compound, the pyrazine rings are facing almost perpendicular to the attached benzene ring, with the internal nitrogen atoms being twisted to point inwards and the distal

nitrogens pointing outwards. The overall shape of this ligand is reflected in the N-C-O-C torsional angle of 6.6°. The distance between the internal nitrogen atoms is 12.210Å, whereas the distal nitrogens have a longer distance of 16.587Å. These less hindered distal nitrogen atoms are more likely to coordinate to metals.

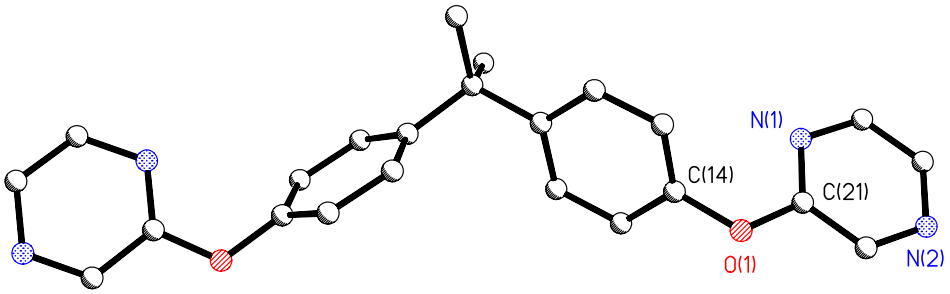
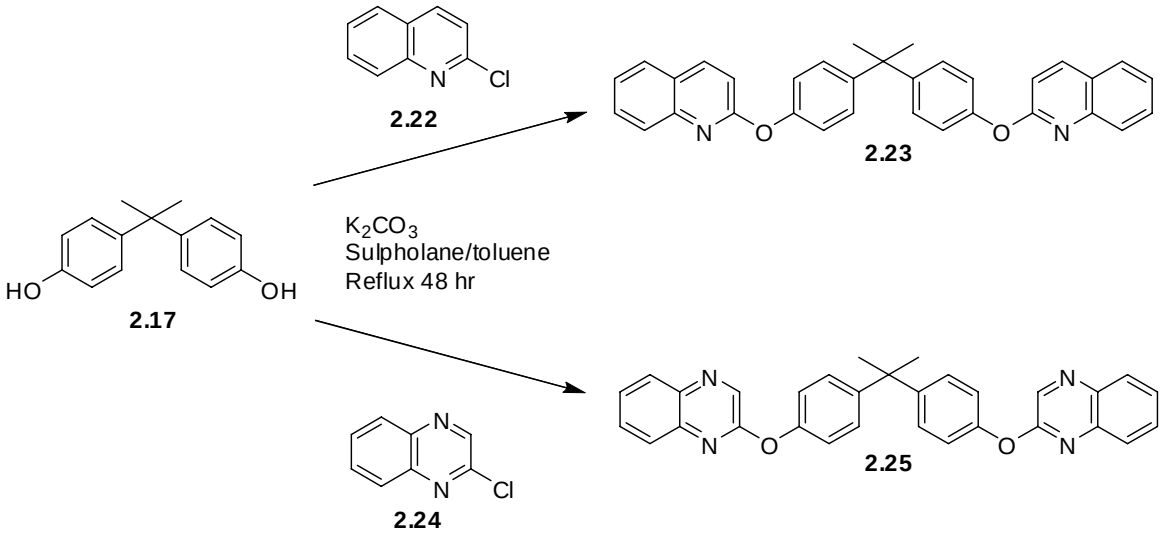


Figure 2.11 - *Crystal structure of ligand **2.21** with hydrogens omitted for clarity. Selected bond lengths (Å) and bond angles (°): C14-O1 1.407(1), O1-C21 1.367(1), C21-N1 1.315(2), C21-O1-C14 118.52(8), N1-C21-O1 120.90(9).*

In the molecular packing there are columns of ligands along the c-axis that are linked by weak edge-to-face interactions. The benzene rings of a ligand in the column edge-to-face π stack with the two benzene rings of another adjacent ligand (2.706Å). To optimize this π-stacking, each ligand has one benzene ring oriented in a facial arrangement and the other in an edge-on arrangement. Furthermore, the facially arranged benzene rings further interact via edge-to-face interactions to adjacent pyrazine rings (2.795Å). No π-π stacking interactions or C-H···π interactions involving methyl hydrogen atoms were observed.

The next two ligands synthesised from ligand precursor **2.17** are outlined in Scheme 2.2. The synthesis outlined in Scheme 2.2 is identical to that shown in Scheme 2.1 for ligands **2.19** and **2.21**. The diaryl ether linkages on ligands **2.23** and **2.25** were synthesised by double nucleophilic aromatic substitution from precursor **2.17** with the haloazines 2-chloroquinoline (**2.22**) and 2-chloroquinoxaline (**2.24**), respectively. Recrystallisation of crude ligands **2.23** and **2.25** from an acetone/water solution gave **2.23** as a white solid in 71% yield and **2.25** as a yellow crystalline solid in 99% yield.

Subsequently, these ligands were fully characterised by elemental analyses, mass spectrometry, melting points and by ^{1}H and ^{13}C NMR.[113]



Scheme 2.2 – *Synthesis of ligands **2.23** and **2.25**.*

Crystals suitable for X-ray crystallography were grown for ligands **2.23** and **2.25** and the X-ray structures of these was determined in order to further investigate their conformations in the solid state.

Crystal structure of ligand 2,2-di(4-(2-quinolyloxy)phenyl)propane, 2.23

Yellow plate-like crystals of ligand **2.23** suitable for X-ray crystallography were obtained by slow evaporation of a dichloromethane solution of the ligand. Ligand **2.23** crystallises in the monoclinic space group $P2_1/c$ with a full molecule in the asymmetric unit. The crystal structure of **2.23** is shown in figure 2.12, where the hydrogen atoms are omitted for clarity. Again, any potential mirror symmetry is lost to ligand **2.23** in the solid state, due to the slight twisting of the phenyl rings about the central quaternary carbon and the different conformations of the quinoline ether units. The quinoline rings are perpendicular to the attached benzene ring, which is clearly depicted in the space-filling diagram illustrated in figure 2.13. The quinoline rings of the ligand are also facing in opposite directions and are considerably tilted away from the mean plane of the benzene rings. The two internal nitrogen atoms point inwards towards the center of

each of the benzene rings, with a separation of 10.141Å. The slightly twisted conformation clearly seen in the ligand is reflected in the bond angles around the oxygen.

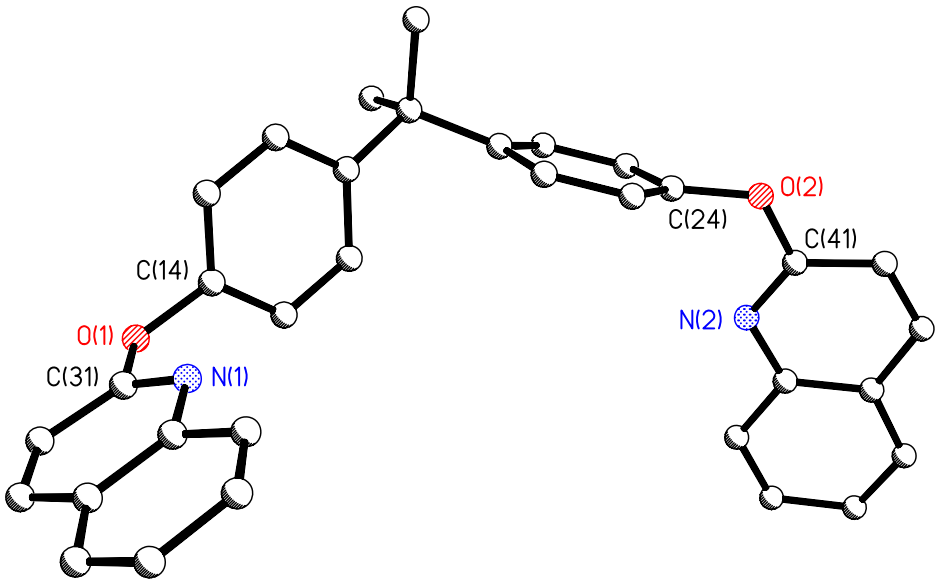


Figure 2.12 - *Crystal structure of ligand* ***2.23*** *with hydrogens omitted for clarity. Selected bond lengths (Å) and bond angles (°): C14-O1 1.415(2), O1-C31 1.376(2), C31-N1 1.305(2), C24-O2 1.412(2), O2-C41 1.374(2), C41-N2 1.306(2), C31-O1-C14 119.0(1), N1-C31-O1 119.7(1), C41-O2-C24 120.3(1), N2-C41-O2 119.7(1).*

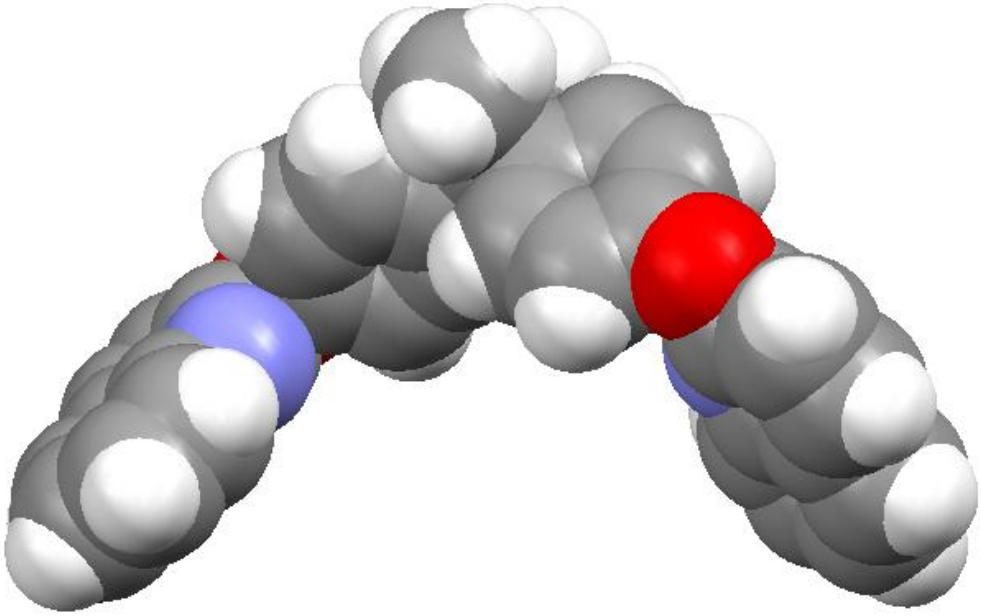


Figure 2.13 - *Space-filling diagram of ligand* ***2.23.***

In the crystal packing, there are two sheets of ligands that lie in the plane of the bc-axes, interacting via edge-to-face interactions. These two sheets lie back to back to each other and do not interact with other layers. The edge-to-face π interactions are between the quinoline rings and benzene rings of ligands that range from 2.656Å to 2.717Å. No π-π stacking interactions were observed.

Crystal structure of ligand 2,2-di(4-(2-quinoxalinyloxy)phenyl)propane, 2.25

Yellow crystals of ligand **2.25** suitable for X-ray crystallography were obtained by slow evaporation of a dichloromethane:methanol solution of the ligand. Ligand **2.25** crystallises in the monoclinic space group $P2_1/n$ with a full molecule in the asymmetric unit. The crystal structure is shown in figure 2.14, where the hydrogen atoms are omitted for clarity.

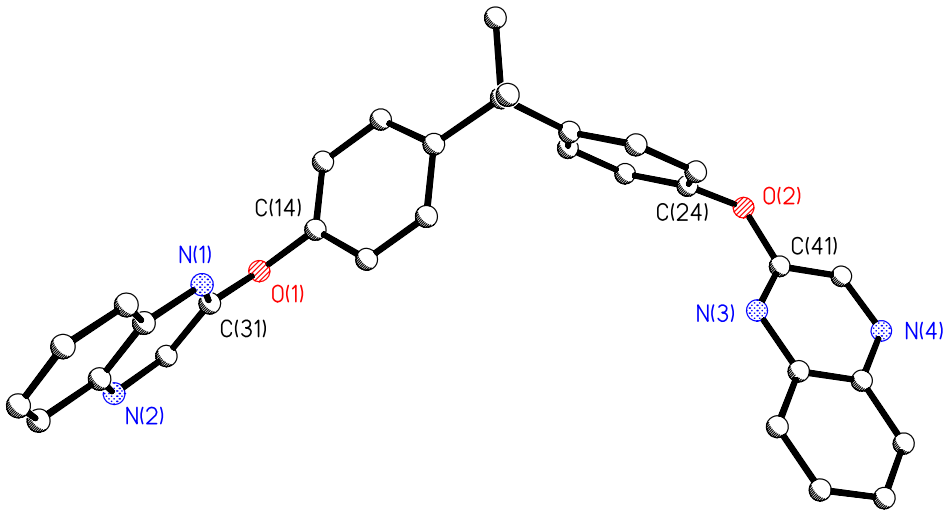


Figure 2.14 - *Crystal structure of ligand* ***2.25*** *with hydrogens omitted for clarity. Selected bond lengths (Å) and bond angles (°): C14-O1 1.413(2), O1-C31 1.368(1), N1-C31 1.305(2), C24-O2 1.411(2), O2-C41 1.367(2), N3-C41 1.300(2), C31-O1-C14 119.29(9), N1-C31-O1 121.4(1), C41-O2-C24 118.83(9), N3-C41-O2 121.2(1).*

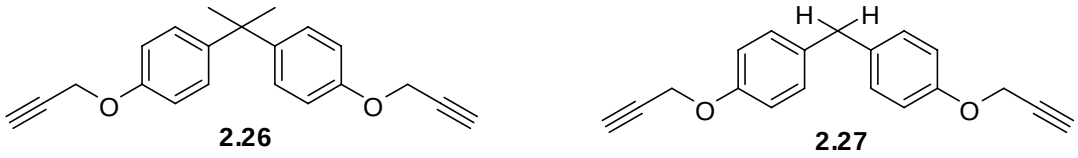
The solid state structure of ligand **2.25** is very similar to that of ligand **2.23**. In fact the only difference between the two structures is the different heterocyclic group. In the solid state, ligand **2.25** has a slight twisting of the two adjacent benzene rings about the central quaternary carbon, as depicted in figure 2.14. The quinoxaline heterocyclic

groups are also perpendicular to the attached benzene groups, both pointing inwards, towards the centre of the benzene rings. The two internal nitrogen atoms also point inwards towards the centre of each of the benzene rings, with a separation of 10.394Å, whereas the distance between the less hindered nitrogens is larger with a value of 14.707Å. The less hindered nitrogens are pointing outwards in the opposite direction to the internal nitrogen atoms and are more likely to bind to metals due to their less hindered environment. On the other hand the internal nitrogens are more hindered, because of the close proximity of the bridging bisphenol group, so are therefore unlikely to coordinate to metals. The slightly twisted conformation seen in the ligand is reflected in the reasonably low N-C-O-C torsional angles of 11.8° and 14.7°.

The packing diagram of **2.25** is made up of strands of ligands that are inter-linked by π-π stacking and edge-to-face interactions. Strands of ligands stack down the a-axis of the unit cell, with π-π stacking interactions between neighbouring quinoxaline rings (3.353Å). Subsequently, strands of adjacent stacks of ligands interact through weak edge-to-face π stacking interactions, with the edge of the quinoxaline oriented towards the face of the benzene rings (2.690Å).

A literature search revealed few compounds that are closely related to ligands **2.19**, **2.21**, **2.23** and **2.25**. There are only a few similar ligands reported in the literature based around a Bisphenol A type core, with the central propane group bridging together two benzenes rings. Figure 2.15 shows some examples of such ligands from the literature that are structurally similar to the Bisphenol A-type ligands and have been used to construct metallosupramolecular species. Ligand **2.26** is similar to the ligands mentioned above having the same bisphenol A-type core with alkyne groups attached instead of nitrogen containing heterocycles. Ligand **2.27** is almost identical to ligand **2.26** with alkyne groups also attached and a central CH_2 group bridging together the two benzenes instead of a propane group. In order to use these two ligands as synthons in metallosupramolecular chemistry, McArdle et al. first converted ligands **2.26** and **2.27** to dialkynyldigold(I) ligand precursors. Reaction of the dialkynyldigold(I) ligands with diphosphine ligands resulted in the self-assembly of simple macrocyclic rings to more complicated [2]catenane complexes.[114-117] McArdle et al. carried out studies on numerous ligands similar to **2.26** and **2.27** with different 'hinge' groups between the two benzene rings. They found that the type of complex formed (ring or catenane) was

dependent on the 'hinge' group of the bisphenol ligand and/or the spacer group in the diphosphine ligand.[115-117]



2.26 **2.27**

Figure 2.15 - *Structurally similar ligands to the Bisphenol A based ligands.*

Figure 2.16 illustrates some examples of ligands that display some structural similarities to the Bisphenol A based ligands. If one removed the central bridging propane group on bisphenol A, one would have a single bond between the two benzene rings, thus creating a 4,4'-biphenol core. Ligands **2.28**-**2.30** are some examples of ligands designed around such a 4,4'-biphenol core with different nitrogen containing heterocycles. Due to the loss of the central propane group the shapes of ligands **2.28**-**2.30** are quite different; however they may still form similar metallosupramolecular assemblies. Ligand **2.28** has the same 2-pyridine units attached to the 4,4'-biphenyl core similar to that of ligand **2.19**. Ligand **2.28** forms a one-dimensional zigzag metallopolymer with $AgNO_3$ and a discrete mononuclear complex in the presence of $CuCl_2$.[118] Ligands **2.29** and **2.30** only differ from ligand **2.28** by having two-atom spacer groups, with either a 2- or 4-substituted pyridine unit attached to the 4,4'-biphenyl core. Ligands **2.29** and **2.30** are reported to form one-dimensional polymeric chains with $AgCF_3SO_3$ and $Co(NO_3)_2$, respectively.[119, 120]

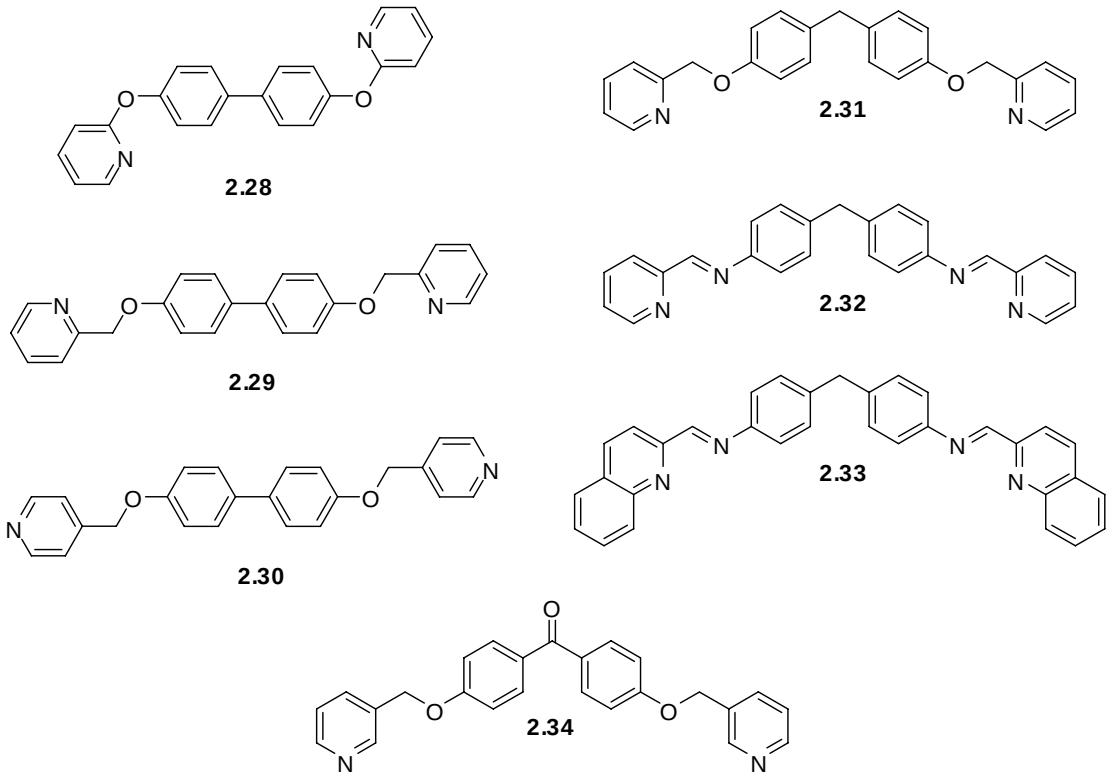


Figure 2.16 – *More examples of structurally similar ligands to the Bisphenol A based ligands.*

Ligands **2.31**-**2.34** are some more ligands that display structural similarities to the Bisphenol A based ligands. Instead of having the central propane group bridging the two benzenes, ligands **2.31**-**2.33** have just a methylene group. Ligands **2.32** and **2.33** are also examples of similar ligands to the Bisphenol A based ligands with different binding domains. These two ligands feature two pyridylimine or isoquinolylimine binding domains as opposed to the nitrogen heterocyles focused on in this thesis. Ligand **2.31** forms a one-dimensional coordination polymer with $AgCF_3SO_3$ and acts as a bis-monodentate ligand linking two silver atoms through the nitrogens.[119] In 1997, Hannon and co-workers reported the reaction of ligand **2.32** with $Ni(BF_4)_2$ resulting in the formation of a dinuclear triple-stranded helicate.[121] The reagents used to synthesise ligand **2.32** are relatively inexpensive, therefore many research groups have been investigating the pyridylimine ligand and its helical complexes. In 2000, Yoshida et al. reported the formation of a dinuclear triple-helical structure with ligand **2.32** and $Zn(ClO_4)_2$.[122] They observed the presence of a small cavity between the three central spacer groups of the ligands; unfortunately the ClO_4^- ions were too large to fit inside

it.[122] Soon after more triple-stranded helicates were prepared from ligand **2.32** with $Co(NO_3)_2$,[123] $FeCl_2$,[124] $Cu(ClO_4)_2$ [125]and *cis*-$[Ru(dmso)_4Cl_2]$.[126] Hannon and co-workers not only synthesised the first diruthenium(II) triple–stranded helicate, but also investigated its potential DNA binding ability and activity against cancer cells.[126] Excitingly, the helicate compared well with that of cis-platin and further detailed DNA-binding and biological studies into this helicate are currently under way. Ligand **2.33** differs from ligand **2.32** by fusion of a benzene ring to each of the pyridine groups and is reported to form a double-helical array with AgOAc.[127] The X-ray structure of the double helix revealed a benzene solvent molecule present in one of the groves of the helix, however the benzene molecule did not interact with neighbouring ligand strands.[127] Ligand **2.33** also generated dinuclear double-stranded supramolecular boxes with $[Cu(MeCN)_4](BF_4)$ and $AgPF_6$ and dinuclear triple-stranded helicates with $Fe(BF_4)_2$ and $NiCl_2$.[128]

Ligand **2.34** is an example of a ligand with quite a different structural core to all of the other ligands described, namely a benzophenone core. Kuroda and co-workers reported the self-assembly of this ligand with $Pd(NO_3)_2$ into a spectacular quadruply-stranded metallohelicate. Furthermore, the quadruply-stranded metallohelicate undergoes spontaneous dimerization to form an interlocked quadruple helicate, in which the interlocked helicate is the thermodynamically stable one and the quadruply stranded helicate is the kinetic product.[129]

All four ligands (**2.19**, **2.21**, **2.23** and **2.25**) outlined above are envisaged as potential building blocks in the construction of metallosupramolecular assemblies. Over the years numerous metallosupramolecular species have been synthesised from ligands containing abundant pyridine rings. 2-, 3- And 4-substituted pyridine rings are readily available and widely used by coordination chemists as the heterocycle of choice in potential ligands due to their ability to form complexes, with novel topologies, with most metals in the periodic table. For this reason ligand **2.19** was designed with a 2-substituted pyridine ring. It is also advantageous for coordination chemists to construct ligands that have heterocycles with multiple binding domains. Multiple binding sites allow greater structural diversity than that given by more simple bridging ligands containing the N-heterocycle pyridine. Pyrazine containing ligands have the ability to potentially bridge two metals to form more complex structures. Supramolecular

structures that coordinate through two nitrogens have been explored with silver(I),[130] copper(I),[131] cadmium(II),[132, 133] cobalt(II) and nickel(II).[133] Pyrazine can also just bind to metals through one of the nitrogens, usually the least hindered nitrogen (located in the 4 position of the pyrazine ring).[106, 134, 135] To further explore its potential, pyrazine was used as another nitrogen containing heterocycle in ligand **2.21**.

By fusing a pyridine or pyrazine ring with a benzene ring in the 5- and 6-position one can create a much larger heterocyclic ring system. Ligands **2.23** and **2.25** were designed around such groups with the quinoline and quinoxaline substituted at the 2-position attached to the Bisphenol A core. These ligands were designed so one can draw comparisons between the pyridine and pyrazine substituted Bisphenol A ligands. One difference is that the quinoline and quinoxaline substituted ligands have a much larger and comparatively bulkier π ring system, which is known to increase the propensity for π-π stacking interactions.[136]

Complexes with ligand 2.19

*Crystal structure of the complex with $CoBr_2$ (**2.35**)*

Ligand **2.19** and cobalt(II) bromide were both dissolved in acetone and the solutions carefully mixed together. Within minutes of standing on the bench big blue block-like crystals grew on the bottom of the vial suitable for X-ray crystallography. Analysis of the crystals revealed an undulating 1-dimensional coordination polymer that crystallised in the orthorhombic space group Pbca. The asymmetric unit contains one ligand molecule, one $CoBr_2$ and an acetone solvent molecule. A small section of the one-dimensional polymer is shown in figure 2.17 with the hydrogens and solvent molecule removed for clarity.

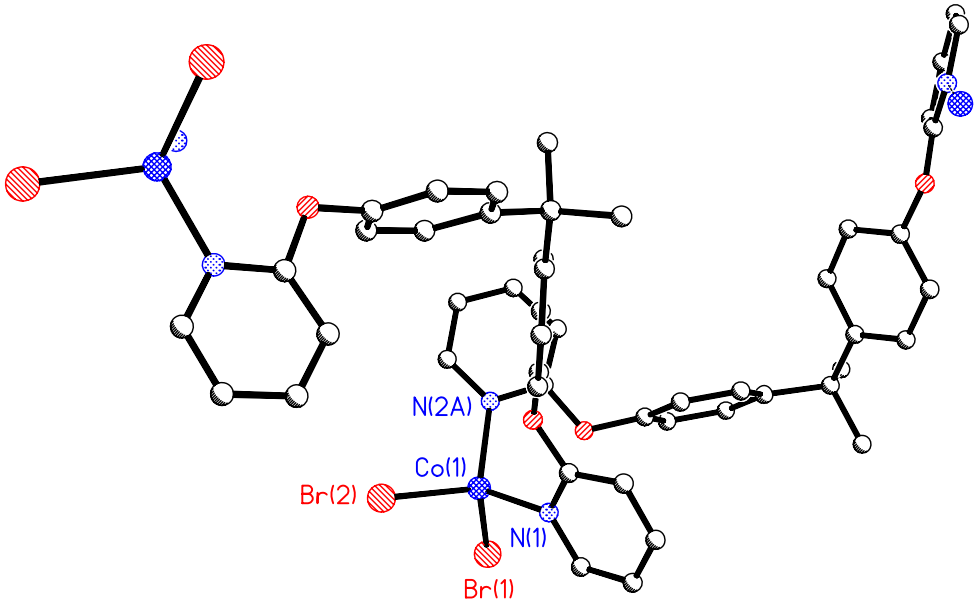


Figure 2.17 – *A section of the one-dimensional coordination polymer* ***2.35****. Selected bond lengths (Å) and angles (°): Co1-N1 2.041(2), Co1-N2A 2.047(2), Co1-Br1 2.388(4), Co1-Br2 2.376(5), N1-Co1-N2A 110.06(8), N1-Co1-Br2 109.75(6), N2A-Co1-Br2 109.16(6), N1-Co1-Br1 105.64(6), N2A-Co1-Br1 110.24(6), Br2-Co1-Br1 111.93(2).*

The cobalt atom is 4-coordinate, being coordinated by pyridine nitrogen atoms of two ligands and two bromide counterions. The coordination geometry of cobalt is approximately tetrahedral with the largest deviation from tetrahedral being 105.6° (N1-Co1-Br1). The Co-N bond lengths are 2.041Å and 2.047Å, which are similar to previously reported bond lengths for comparable compounds. The conformation of the ligand in complex **2.35** is similar to that of the free ligand **2.19** in some aspects and quite different in others. The pyridine binding arms of the ligand are again perpendicular to the attached benzene rings, with the nitrogen atoms now being twisted to point outwards in one direction. This is in comparison to the crystal structure of ligand **2.19**, which showed the two pyridine nitrogen atoms pointing inwards, towards the central cavity between the two benzene rings. Complex **2.35** adopts a different conformation in the pyridine binding arms in order to accommodate the geometric constraints on the cobalt atom.

The polymer propagates in an undulating wave-like fashion in one dimension along the a-axis. In one direction the polymer looks like square stepped waves that rise and fall, hence the overall undulating effect. A larger section of the polymer illustrating the

undulating wave-like effect is depicted in figure 2.18, with the hydrogens and solvent molecules omitted for clarity. Each ligand bridges two cobalt atoms with the cobalt atom binding to two bromide counterions and two pyridine nitrogens. Each ligand also acts as an 'L' shaped bridge with the cobalt atom connected to two such ligands related by a 2-fold screw axis. The 'L' shaped ligand flips orientation between cobalt atoms, so that each cobalt atom is coordinated to a pyridine ring above and a pyridine ring below it. As a result, the ligands alternate in orientation along the chain to give an undulating stepped polymer, as shown in figure 2.18.

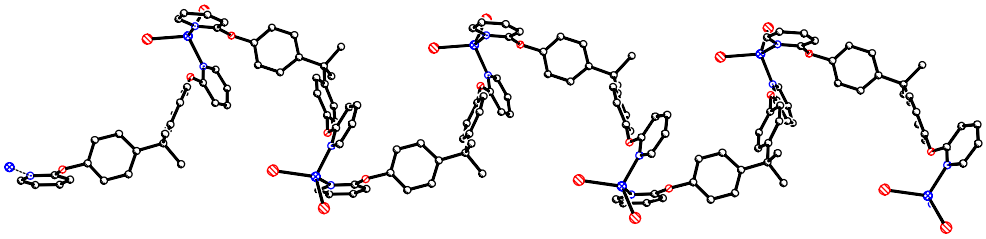


Figure 2.18 – *A larger section of the one-dimensional polymer of* ***2.35*** *illustrating the undulating wave-like effect.*

In the packing of **2.35** the one-dimensional polymers are stacked offset to each other. Consequently, there are no π-π stacking interactions between polymer strands in the extended structure and very few other interactions between adjacent polymer strands. However, there are some close hydrogen bonding interactions between various hydrogens of the ligand molecules and bromine atoms of adjacent polymer strands (2.917Å-3.037Å). The undulating wave-like orientation of the polymer gives pockets that are filled by acetone solvent molecules in the extended structure. These acetone solvent molecules interact extensively with polymer strands through hydrogen bonds and other short contacts. Acetone solvent molecules hydrogen bond to bromine atoms in the main structure, with distances of 2.923Å and 2.947Å. The solvate acetone oxygen also has short contacts of 2.456Å and 2.567Å to pyridine hydrogens of adjacent ligand molecules.

*Crystal structure of the complex with $CoCl_2$ (**2.36**)*

Ligand **2.19** and cobalt(II) chloride were both mixed in acetone and combined. Blue block-like crystals were obtained within minutes of mixing, which were suitable for X-ray crystallography. The complex crystallises in the monoclinic space group C2/c, with

half a ligand molecule, half a $CoCl_2$ and half an acetone solvent molecule in the asymmetric unit. X-ray analysis revealed an interesting one-dimensional helical coordination polymer. A small section of this one-dimensional helical polymer is shown in figure 2.19 with the hydrogens and acetone solvent molecule removed for clarity.

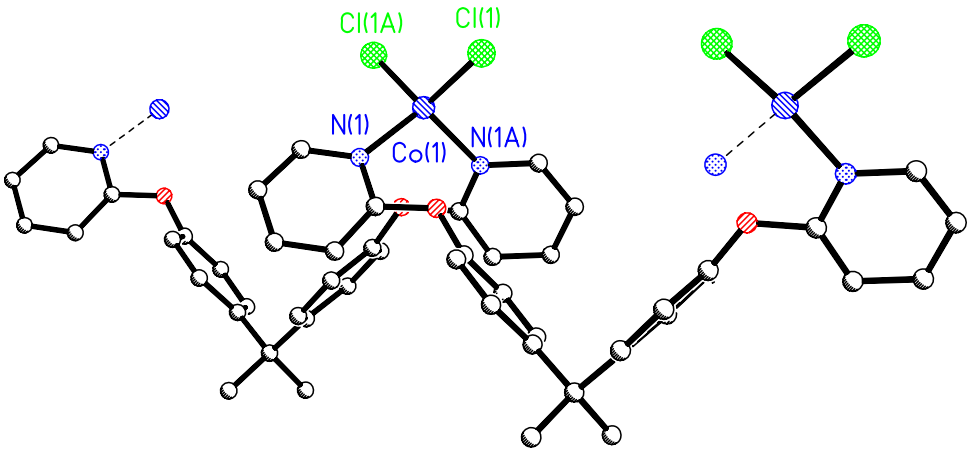


Figure 2.19 - *A section of the one-dimensional helical coordination polymer* ***2.36****. Selected bond lengths (Å) and angles (°): Co1-Cl1 2.2292(6), Co1-N1 2.055(2), N1-Co1-N1A 106.95(8), N1-Co1-Cl1 113.71(5), N1-Co1-Cl1A 104.17(4), N1A-Co1-Cl1 104.17(4), N1A-Co1-Cl1A 113.71(5), Cl1A-Co1-Cl1 114.18(4).*

Scientists have been fascinated with helical coordination polymers and arrays over the last 20 years. Helical arrays are not just limited to helices that are arranged by metal ions. In fact helices have been observed in many biological systems in nature, the most famous of which is the double-helical structure of DNA. Inorganic chemists describe complexes in which ligands that coordinate around a metal ion in a helical manner as 'helicate', where the word 'helicate' is derived from the word *helix*[137] (meaning a three-dimensional spiral curve such as a spring) and suffix *–ate*. Thus in chemical terms a helicate is described as the wrapping of ligand strands around metal ions about a central helical axis.[40-43]

There are a couple of requirements placed on the ligand in order to be able to construct helical architectures compared to other non-helical arrays. The ligands must first have at least two binding domains for coordination to metal ions and be flexible enough to wrap around the metal ions in a helical manner. In supramolecular chemistry the helicity of

the array is also influenced by coordination to various metal ions and other weaker interactions such as π-π stacking interactions and hydrogen bonding. Over the years numerous single-, double-, triple- and quadruple-stranded helicates have been reported in the literature.[42, 43, 138]

Helical coordination polymers prepared from achiral starting materials generally form in centric space groups and contain a racemic 1:1 mixture of both left (M) and right-handed (P) helices to give an internal racemate. The 'M' and 'P' helices are non-identical mirror images of each other and can therefore not be superimposed on top of one another. To distinguish between different helices one must view the helix down its helical axis. If the helix rotates in a clockwise direction away from the observer when viewed down its helical axis it is termed a right-handed 'P' helix. Conversely, if the helix rotates in an anti-clockwise direction away from the observer when viewed down the helical axis it is called a left-handed 'M' helix. The terms 'P' and 'M' refer to 'plus' and 'minus' respectively.[42, 43, 138, 139] A schematic illustrating the left- and right-handed helices is depicted in figure 2.20.[43] Helices also have what is known as a 'pitch', which is the distance it takes for the helicate strands to do a full 360° turn along the helical axis. In this thesis the pitch of various one-dimensional helical polymers was found to traverse between the metal atoms.

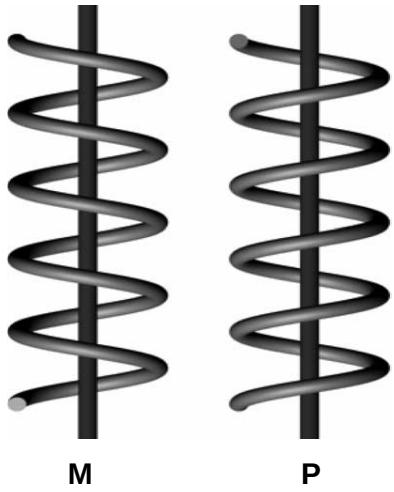


Figure 2.20 – *Schematic representation of M(-) and P(+) helices.*

In the helical complex **2.36** the cobalt atom is 4-coordinate, being coordinated by pyridine nitrogen atoms of two ligands and two chloride counterions. The coordination geometry of cobalt is distorted tetrahedral with the largest deviation from tetrahedral

being 104.2° (N1-Co1-Cl1A). The cobalt metal atom in complex **2.36** has a more distorted tetrahedral geometry than that of the previous one-dimensional polymer (**2.35**) formed from cobalt bromide. This may be due to the helicity induced upon complex **2.36** as the ligand strands wrap around the cobalt atoms resulting in a distortion from tetrahedral. The Co-N bond length is 2.055Å and the Co-Cl bond length is 2.229Å, which are both within the normal range. The pyridine binding arms of the ligand are once again perpendicular to the attached benzene rings, with the nitrogen atoms now turned slightly outwards in order to coordinate to the metal atoms.

The complex has two-fold rotation axes that pass through the cobalt atom and central quaternary carbon (C1) of the Bisphenol A backbone to generate a one-dimensional helical polymer that propagates down the c-axis. The ligand is achiral and belongs to a centrosymmetric space group, and therefore the structure must contain a 1:1 racemic mixture of both M- and P-handed helices that are related by a centre of symmetry. The P-enantiomer of the helix is shown in figure 2.21, with the hydrogens and solvent molecules removed for clarity. The helices have a pitch of 11.866Å, which is equal to the length of the c-axis. A schematic representation of the pitch in complex **2.36** is also detailed in figure 2.21. In this particular case the pitch distance corresponds to the distance between two cobalt atoms that are coordinated to a ligand molecule in the helical chain.

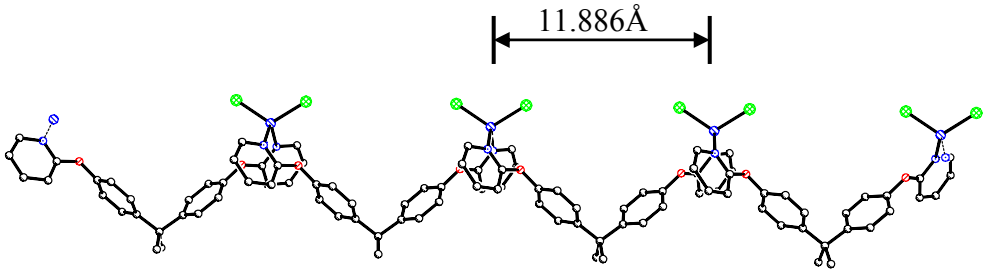


Figure 2.21 – *A perspective view of the right-handed P-enantiomer helical chain of* ***2.36****. The pitch, which is the distance it takes for the helicate strands to do a full 360° turn along the helical axis, is also indicated.*

There is half an acetone molecule in the asymmetric unit which is disordered about a centre of inversion. These acetone solvent molecules fill the voids in the crystal lattice

through extensive hydrogen bonding interactions with helical strands. In the packing adjacent helices are mainly stitched together by C-H···Cl interactions between chlorine atoms and pyridine hydrogens of the ligands (2.879Å). No other significant interactions were observed.

*Crystal structure of the complex with $CuCl_2$ (**2.37**)*

Slow evaporation of a solution containing ligand **2.19** and copper(II) chloride produced green plate-like crystals after standing for a week. The crystals extinguished perfectly and were found to be suitable for X-ray crystallography. The complex crystallises in the monoclinic space group C2/c, with one ligand molecule, one $CuCl_2$ and one dichloromethane solvent molecule in the asymmetric unit. The asymmetric unit is shown in figure 2.22 with the hydrogens and solvent molecule removed for clarity.

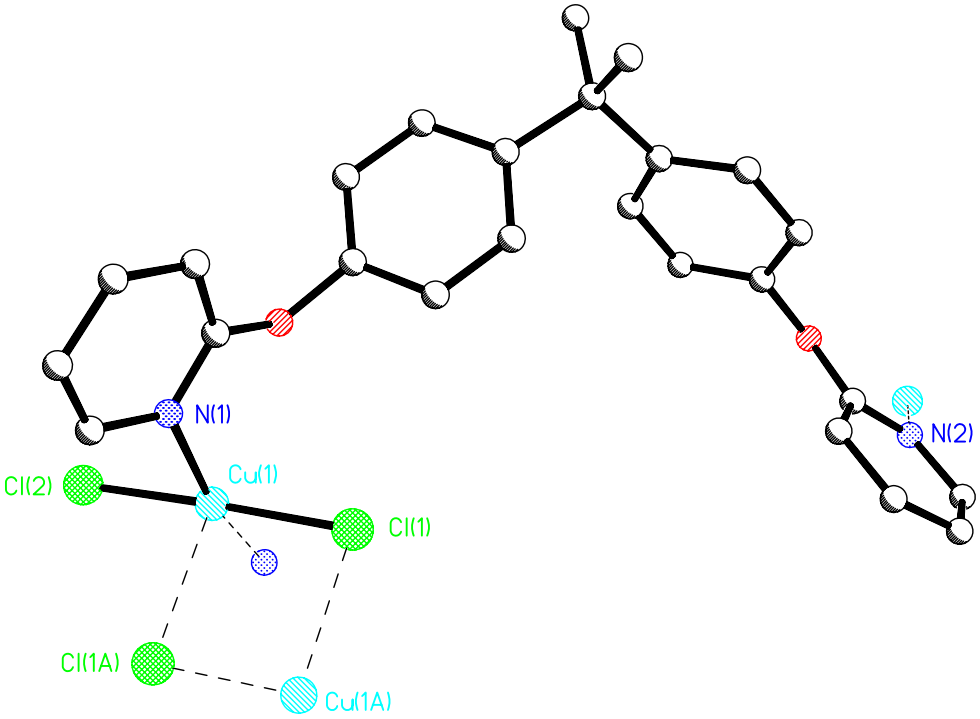


Figure 2.22 – *Contents of the asymmetric unit of complex **2.37**. Selected bond lengths (Å) and bond angles (°): Cu1-N1 2.015(2), Cu1-N2 2.004(2), Cu1-Cl1 2.3526(6), Cu1-Cl2 2.2768(6), Cu1-Cl1A 2.7323(6), N1-Cu1-N2 167.08(7), N1-Cu1-Cl2 90.48(5), N2-Cu1-Cl2 90.38(5), N1-Cu1-Cl1 91.61(5), N2-Cu1-Cl1 87.75(5), Cl1-Cu1-Cl2 177.76(2), N1-Cu1-Cl1A 96.29(5), N2-Cu1-Cl1A 96.47(5), Cl1-Cu1-Cl1A 84.0(2), Cl2-Cu1-Cl1A 94.99(2), Cu1-Cl1-Cu1A 96.0(2).*

The pyridine binding arms of a ligand are still facing in opposite directions away from one another and are considerably tilted away from the mean plane of the benzene rings. Also, the pyridine rings are perpendicular to the attached benzene rings, as seen previously in the crystal structure of ligand **2.19** itself. The two nitrogen atoms of each of the pyridine binding arms are now pointing in opposite directions away from the central cavity between the two benzene rings. This is in comparison to the crystal structure of ligand **2.19**, which showed the two pyridine nitrogen atoms pointing inwards, towards the central cavity between the two benzene rings. A section of the resulting polymer is shown in figure 2.23, which clearly depicts the overall connectivity of the complex.

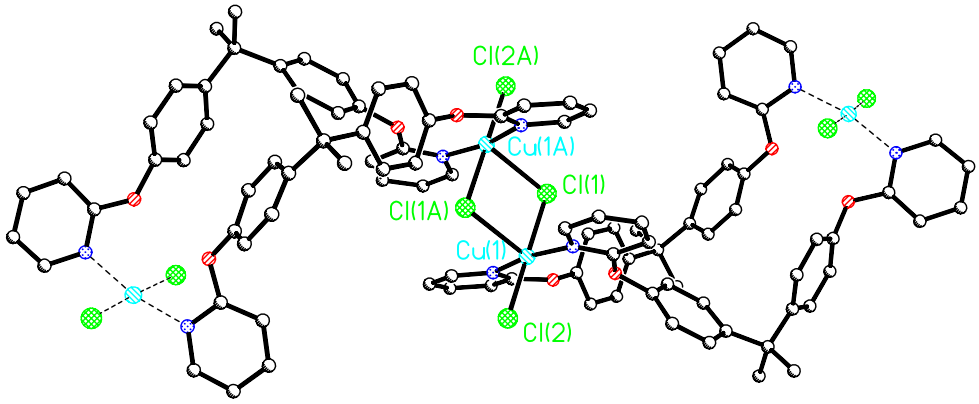


Figure 2.23 – *Perspective view showing a section of the one-dimensional necklace polymer and the Cu_2Cl_4 square.*

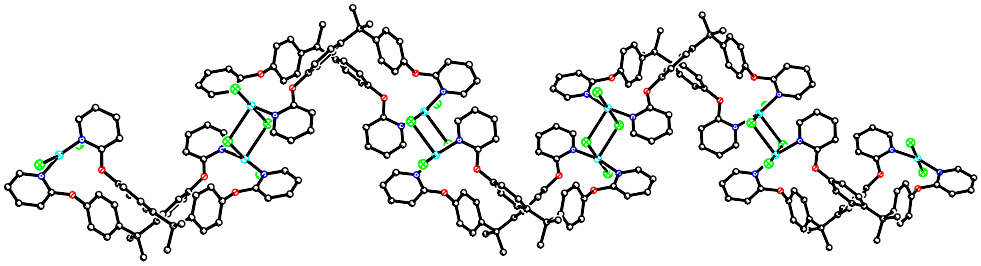
The copper atoms of **2.37** have a square-pyramidal environment binding to one terminal chlorine atom, two bridging chlorine atoms and the nitrogen atoms of two separate ligands. Two nitrogens from the pyridine ligands and two of the chlorine atoms form the N_2Cl_2 basal plane with *trans* geometry. The apical position is occupied by one of the bridging chlorine atoms. The copper atoms are further bridged by two chlorine atoms to form a Cu_2Cl_4 square motif. This Cu_2Cl_4 square motif is quite common for copper chloride complexes. The distance between copper atoms in the square is 3.787Å. This Cu···Cu distance is slightly longer than the average value of 3.492Å found for similar 5-coordinate systems joined by Cu_2Cl_4 squares in the *Crystallographic Structural Database* (CSD; Version 1.10, March 2008). The basal bond lengths for the copper to pyridine nitrogens are 2.015Å and 2.004Å, while the basal bond lengths for

the copper to chlorine atoms are 2.353Å and 2.277Å. These observed basal bond lengths are in the middle of the range for similar bond lengths found on the *Crystallographic Structural Database*.[140-146] The bridging chlorine atom in the apical position has a significantly longer bond length of 2.732Å (Cu1-Cl1A), as is usual for square-pyramidal structures.

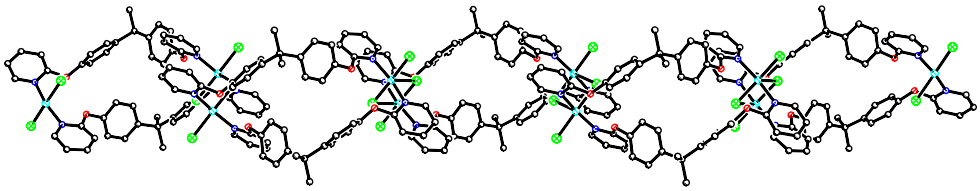
The resulting complex is a 'necklace'-like polymer, which is a one-dimensional polymeric chain made up of M_2L_2 macrocyclic units linked by Cu_2Cl_4 squares. The 'necklace' topology is shown in figure 2.23, with a clearer view of the Cu_2Cl_4 square motif. The two halves of the macrocyclic unit are related by a two-fold rotation axis. Each macrocyclic unit is made up of two ligands bound to two coppers in an almost linear fashion resulting in a 32-membered M_2L_2 macrocycle. The distance between copper atoms in a macrocycle is 12.048Å. Each M_2L_2 macrocyclic unit is concave, which is accentuated by the 'V' shaped conformation of the ligands, as described previously. Unfortunately, individual M_2L_2 macrocycles do not host any guest molecules due to the volume inside the macrocycle being reduced due to the conformation and orientation of the two ligands. The M_2L_2 macrocyclic units flip orientation between the bridging Cu_2Cl_4 squares, so that each Cu_2Cl_4 square is coordinated to a macrocyclic unit above and a macrocyclic unit below it. As a result, the M_2L_2 macrocyclic units alternate in orientation along the chain to give an undulating 'necklace'-like polymer.

If one looks side-on at the complex, the M_2L_2 macrocycle units propagate in an alternating coil-like zigzag fashion with one macrocycle facing up and one macrocycle facing down along the chain. This coil-like formation is translated down the necklace chain with each of the macrocycles inter-linked by Cu_2Cl_4 squares that lie perpendicular to the adjoining macrocycles. A side-on view of the necklace polymer illustrating this is depicted in figure 2.24(a). Figure 2.24(b) shows another view of the necklace polymer when looking from above. This birds eye view of the polymer clearly depicts a continuous chain of large rings (the M_2L_2 macrocycles) connected by smaller rings (the Cu_2Cl_4 squares). This type of topology is similar to that of a necklace, which is why the complex is called a 'necklace' polymer. In fact, the chain of **2.37** looks like that of a belcher chain necklace. A picture of a silver belcher chain necklace is illustrated in figure 2.25. A belcher necklace consists of rings that are interlinked along a chain in an

alternating fashion with neighbouring rings in a chain perpendicular to each other, as depicted in figure 2.25. This style is very similar to complex **2.37**; the only difference is that complex **2.37** has two different sized rings inter-linked in an alternating fashion along the chain.



(a)



(b)

Figure 2.24 – ***(a)*** *Side on view of the copper necklace polymer.* ***(b)*** *Birds eye view of the necklace polymer when viewed from above.*

Figure 2.25 - *A picture of a silver belcher chain necklace.*

The coil-like arrangement of macrocyclic units in complex **2.37** allows the formation of small grooves in the curvature of each macrocycle, as depicted in figure 2.24. These groves are just the right size for the encapsulation of a dichloromethane solvate molecule. The dichloromethane molecule interacts within the groove of each macrocycle through hydrogen bonding interactions to the pyridine rings (2.596Å). There are also short contacts between the chlorine atoms of the solvate molecule to the benzene rings (2.969Å) in the groove of each macrocycle.

In the crystal packing necklace chains pack with numerous interactions between them. There are no π-π stacking interactions between benzene rings within a macrocyclic unit, because of the conformation and orientation of the ligands with respect to each other. The necklace strands stack with weak edge-to-face π stacking interactions between benzene rings and pyridine rings (2.611Å) of adjacent strands. Terminal chlorine atoms interact with hydrogen atoms of pyridine rings on adjacent necklace strands, with the shortest Cl···H interaction being 2.926Å.

*Crystal structure of the complex with $Cu(NO_3)_2$ (**2.38**)*

A solution of copper nitrate dissolved in acetone was layered upon a chloroform solution of ligand **2.19**. Slow evaporation of this solution to dryness produced blue crystalline plates that were suitable for X-ray crystallography. The complex crystallises in the centrosymmetric triclinic space group P-1 to form a dimeric M_2L_2 macrocycle. The asymmetric unit contains one ligand molecule, one copper atom, two coordinated nitrate counterions and partially occupied acetone and chloroform solvent molecules. Figure 2.26 shows a picture of the dimeric M_2L_2 macrocycle with the hydrogens and solvent molecules removed for clarity. The acetone and chloroform molecules occupy the site with 50% occupancy.

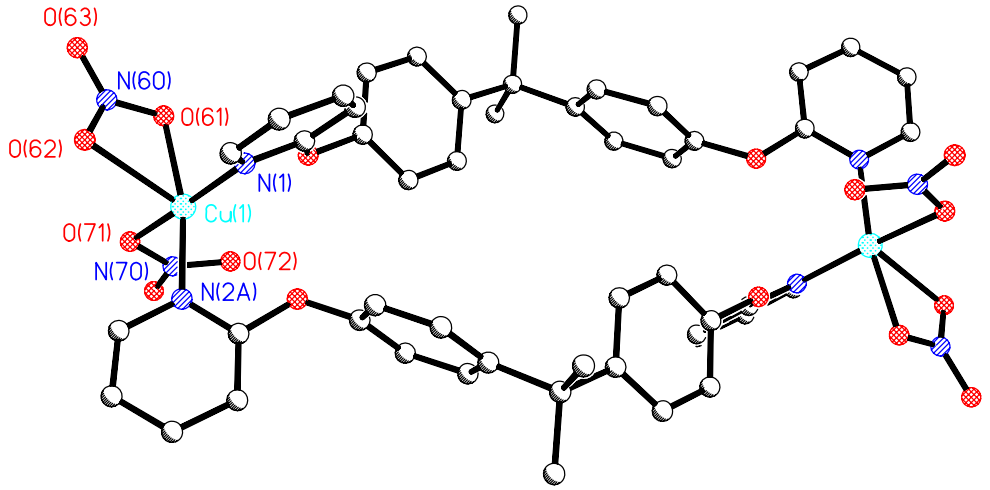


Figure 2.26 – *Perspective view of the dimeric M_2L_2 macrocycle* ***2.38****. Selected bond lengths (Å) and bond angles (°):Cu1-N1 2.006(3), Cu-N2A 1.988(3), Cu1-O61 2.002(3), Cu1-O62 2.405(3), Cu1-O71 1.991(3), N2A-Cu1-N1 95.1(1), O61-Cu1-N1 89.0(1), O71-Cu1-N1 174.3(1), N2A-Cu1-O61 167.6(1), N2A-Cu1-O71 89.5(1), N2A-Cu1-O62 110.0(1), O71-Cu1-O62 90.6(1), O61-Cu1-O62 58.1(1), O71-Cu1-O61 87.1(1), N1-Cu1-O62 90.9(1).*

Each copper atom is 5-coordinate, binding to two pyridine nitrogens, one monodentate nitrate anion and a chelating nitrate anion. The geometry of the copper atom is square-pyramidal, with the two nitrogens from the pyridine ligands and two of the nitrate anion oxygens forming the N_2O_2 basal plane. The two oxygens that reside on the basal plane come from the monodentate nitrate anion (O71) and the chelated nitrate anion (O61). The apical site is occupied by the other chelated nitrate oxygen (O62). The monodentate nitrate anion coordinates to the copper atom through one oxygen atom with a Cu-O bond length of 1.991Å. The other nitrate anion chelates to the copper atom through two oxygen atoms with bond lengths of 2.002Å and 2.405Å. The chelating oxygen nitrate in the apical position has a significantly longer bond length of 2.405Å. There is also a much weaker interaction between the copper atom and the other oxygen of the monodentate nitrate anion of 2.506Å (O72). Overall, these Cu-O bond lengths are similar to structurally similar complexes with the same CuN_2O_3 motif.[147-149] The Cu-N bond lengths of 2.006Å and 1.998Å are also similar to closely related complexes.[147-149]

The dimeric structure consists of two ligand molecules that are bridged by two copper atoms to give a 32-membered macrocycle. Two asymmetric units about a

crystallographic centre of inversion combine to give the M_2L_2 macrocycle, as depicted in figure 2.26. The pyridine binding arms of the ligand lie on opposite sides of the 'V'-shaped Bisphenol A backbone slightly twisting around in order to coordinate to the copper atoms. There is a slight twisting of the benzene rings from coplanar around the central quaternary carbon and the pyridine binding arms are once again nearly perpendicular to the attached benzene rings. Each of the L shaped ligands bridges two copper atoms with a 'V'-shaped bend in the ligand backbone that creates a square shaped dimeric complex. The distance between copper atoms across is 14.145Å (Cu1-Cu1A) and the distance between the central quaternary carbons is 9.190Å (C1-C1A).

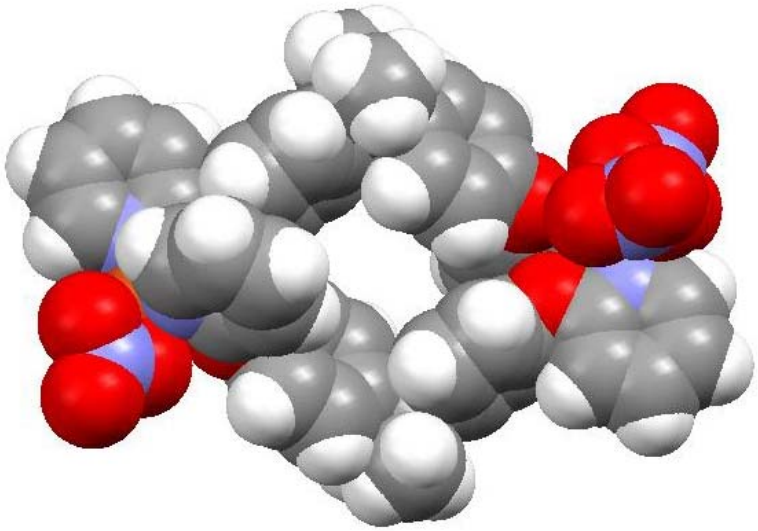


Figure 2.27 – *Space-filling diagram of complex* ***2.38*** *illustrating the void in the central cavity of the* M_2L_2 *dimer.*

There is a small void in the centre of the structure as a consequence of the 'V'-shaped entwining of the ligands. The void is seen more clearly in a space-filling diagram, shown in figure 2.27. Unfortunately, this internal cavity does not play host to any guest molecules, because it is too small.

The oxygen atoms of the coordinated nitrate counterions are involved in numerous C-H···O interactions with both aromatic and methyl hydrogens from the ligand, with distances ranging between 2.523Å-2.684Å. The macrocycles pack together with edge-to-face π interactions between benzene rings and pyridine rings of adjacent dimers (2.707Å). These interactions occur between the edges of pyridine rings to the facially

arranged benzene rings. The solvent molecules also interact extensively with the oxygen atoms of the nitrate counterions and hydrogens from the ligand to fill spaces in the crystal lattice.

*Crystal structure of the complex with $Cu(NO_3)_2$ (**2.39a**)*

A methanol solution of copper nitrate was carefully layered upon a solution of ligand **2.19** dissolved in dichloromethane. Slow evaporation of the blue solution over a couple of weeks furnished beautiful blue crystalline plates suitable for X-ray crystallography. It was first thought that these crystals would give the same dimeric M_2L_2 macrocycle as discussed in the last experiment (**2.38**), because the same ratio of metal to ligand (2:1) was used. However, a completely new complex was made with an intriguing M_2L_4 stoichiometry. In fact X-ray analysis revealed the complex to be a fascinating copper dinuclear quadruple helicate, which are highly topical at the moment. In this experiment the same metal to ligand ratio of 2:1 was used, but with a different solvent.

Unfortunately, the beautiful blue crystalline plates were very air sensitive and began to crack and decompose almost immediately once out of solvent. Although the crystal was mounted as quickly as possible onto the diffractometer, some of the diffraction patterns were weak and showed signs of the crystal being twinned. This was surprising, because initially under the microscope the crystals appeared to be perfect looking plates. However, the crystals were later found to be highly twinned with crystal plates stacked in near perfect alignment on top of each other. On closer examination of other crystals in the vial it was noticed that some of the crystals had a stepped formation indicative of the plates aligned on top of each other. Due to poor quality data and twinning the structure only refines to an R_1 value of 12.79%. A contributing factor to this high R_1 value is the severe disorder seen in the nitrate anions and solvent molecules in the crystal structure. This makes the location and exact description of these anions and solvent molecules impossible. Despite all these problems a solution for the structure was obtained and the crystal structure can be described.

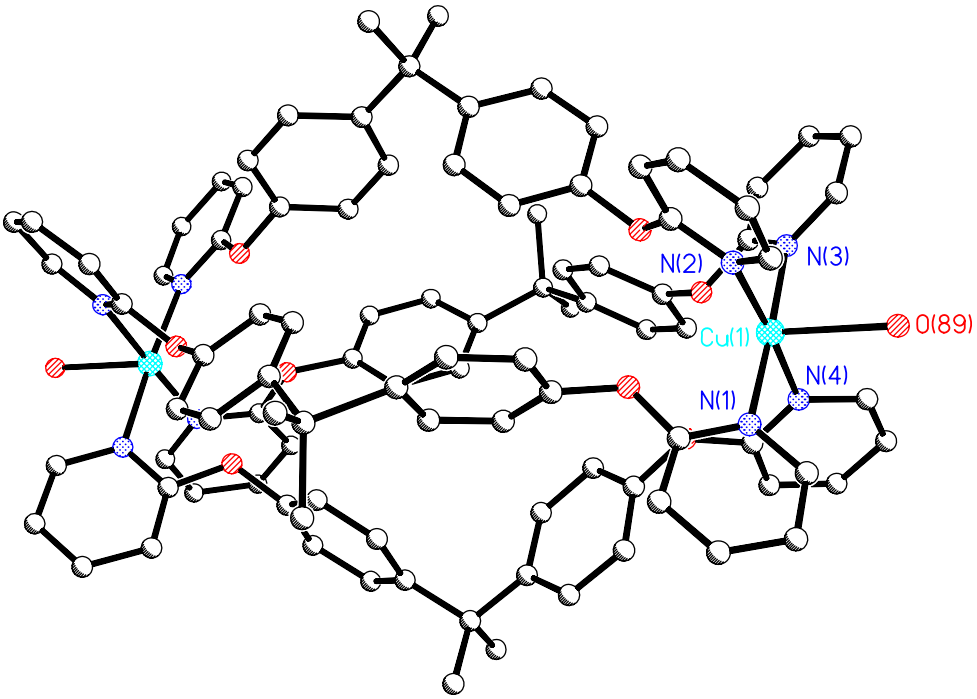


Figure 2.28 – *Perspective side on view of the discrete M_2L_4 copper dinuclear quadruply-stranded helicate (**2.39a**). Selected bond lengths (Å) and bond angles (°):Cu1-N1 2.028(6), Cu1-N2 2.043(7), Cu1-N3 2.019(6), Cu1-N4 2.049(7), Cu1-O89 2.355(6), N1-Cu1-N2 89.6(3), N1-Cu1-N4 89.5(3), N2-Cu1-N4 176.2(2), N3-Cu1-N1 178.0(2), N3-Cu1-N2 90.4(3), N3-Cu1-N4 90.3(3), N1-Cu1-O89 91.1(2), N2-Cu1-O89 91.6(2), N3-Cu1-O89 91.0(2), N4-Cu1-O89 92.1(2).*

The space group is different to **2.38** and the copper dinuclear quadruple helicate solved in the centrosymmetric monoclinic space group C2/c. The asymmetric unit contains four half ligand molecules, one metal atom and water. There are also four highly disordered nitrate counterions and solvent molecules surrounding the helicate. The four nitrogen-bound ligand molecules and water molecule are bound to the copper atom in the asymmetric unit. The two halves of the molecule are related by a two-fold rotation axis that passes through the quaternary carbons of two of the ligands. A picture of the discrete structure is illustrated in figure 2.28, with the hydrogens, disordered nitrate anions and solvent molecules removed for clarity.

Each of the copper atoms has a square-pyramidal geometry coordinated to the nitrogen atoms of four separate ligands and an oxygen atom. Four nitrogens from the pyridine ligands reside on the basal plane and the apical position is occupied by a water molecule. The equatorial Cu-N bond lengths range between 2.019Å to 2.049Å. The

water molecule on the apical site coordinates to the copper atom with a Cu-O bond length of 2.355Å. The cage-like complex has a distance between copper atoms of 13.320Å. The other dimensions of the cage are defined by the distance between the central quaternary carbon atoms of opposing ligands, with lengths of 10.558Å (C1-C40) and 10.814Å (C21-C61). There is a twisting of the two benzene rings about the central quaternary carbons of the ligand strands and the pyridine rings are also approximately perpendicular to the planes of the attached benzene rings, which allow the pyridine rings to wrap around the copper atoms in a helical fashion. The observed conformation of the ligand in complex **2.39a** is similar to that seen in the other crystal structures discussed so far in this thesis. There is a small void inside the cavity of the helicate. However, due to the orientation of the ligand strands along the helical axis it is not a large enough void to encapsulate any guest molecules for potential host-guest interactions.

The helical nature of the ligands is more clearly seen when viewed down the Cu-Cu axis, as shown in figure 2.29. The helical pitch of **2.39a** is defined by the approximate 90° angle of each ligand with respect to each other about the helical axis. This complex exhibits an approximate D_4 symmetry and can be classified[40] as an unsaturated helicate, because the copper atoms require a supplementary water molecule to satisfy the metal's coordination requirements. Complex **2.39a** is also classified[40] as a homostranded homotopic quadruple helicate, since all the coordinated ligand strands are identical and each has the same binding domains. The space group is centrosymmetric C2/c, therefore the structure must contain a 1:1 racemic mixture of both helices and mirror image molecules with the opposite twist are present in the crystal structure, that is a racemic mixture of both M- and P-handed helices that are related by a centre of symmetry.

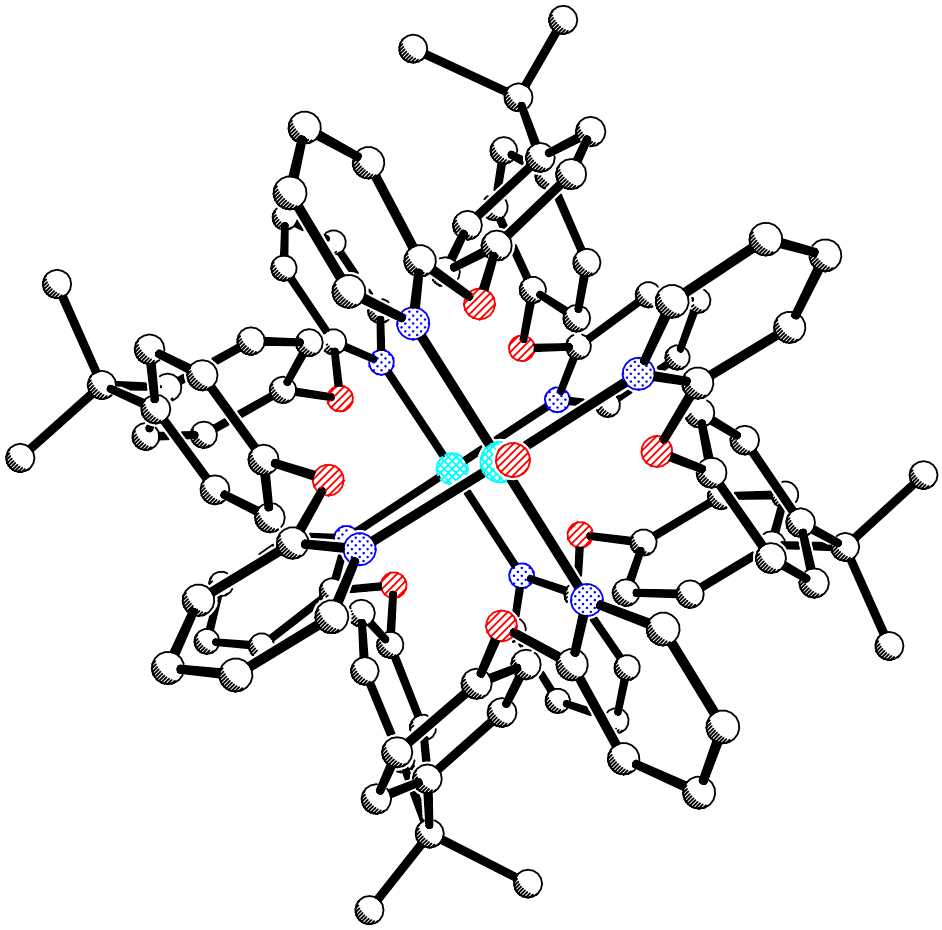


Figure 2.29 – *View of complex **2.39a** looking down the helical c-axis of the copper atoms.*

To date single-, double- and triple-stranded helicates have been well documented in the literature. Reports of quadruply-stranded helicates were only first reported in the literature in 1997-1998. In fact one of the first saturated, quadruply-stranded helicates was synthesised by David McMorran, a past member of the Steel group and has previously been discussed earlier in this chapter. McMorran et al. described the self-assembly of the first saturated quadruply-stranded helicate generated from ligand **2.8** and a palladium precursor.[103] This intriguing quadruply-stranded helicate was found to reversibly encapsulate complex anion guests, such as perchlorate. In 1997, Peng and co-workers reported an unsaturated quadruply-stranded helicate composed of a pentanuclear cobalt or nickel chain of metal atoms that have four pentadendate ligands wrapped around in a helical manner.[150] Peng and co-workers also described the formation of a similar quadruply-stranded helicate with $CrCl_2$, composed of a heptanuclear chain of metal atoms with four ligands wrapped around inducing

helicity.[151] These two helicates synthesised by Peng and co-workers can be classified as unsaturated helicates, because the metal ions require supplementary ligands, such as metal-metal bonds and ancillary ligands, to satisfy the requirements of the octahedral metal ions. This is opposed to saturated helicates in which the metal coordination is satisfied by the binding domains of the ligand strands.

In 2000, a few quadruply-stranded helicates were reported in the literature, using ligands shown in figure 2.30. Castro et al. reported the formation of a barium dinuclear quadruple helicate with ligand **2.40** that was formed by two interlocked metallomacrocycles bound to two barium atoms through their terminal ketoesters.[152] Also, an impressive silver quadruple helicate was synthesised by Lehn and co-workers from $AgCF_3SO_3$, composed of ten silver atoms surrounded by four pentatopic **2.41** molecules.[153] Chiral ligand **2.42** yields a quadruply stranded helicate with $CuCl_2$ in dichloromethane that has a single chloride anion encapsulated in the cavity of the cage.[154] This complex and others have also been used as Lewis acids for asymmetric catalysis. A unique iron dinuclear quadruple helicate was synthesised from ligand **2.43**, which is comprised of four ligands that were linked by oxygen atoms to the chloride bridged iron(II) metal centers.[155]

In 2004, Bassett et al. reported the formation of several dinuclear helical complexes with various lanthanides.[156] A quadruple-stranded dinuclear europium helicate with ligand **2.44** was also reported; however despite numerous attempts they were unable to crystallise the complex. Raymond and co-workers reported the first two examples of bisbidentate quadruple-stranded helicates with ligands **2.45** and thallium(IV).[157] Both complexes have two capped square-antiprismatic thallium(IV) centers coordinated to four bisbidentate ligand chelate strands with a helical twist. Most recently, Kuroda and co-workers reported the self-assembly of ligand **2.34** with $Pd(NO_3)_2$ into a spectacular quadruply-stranded metallohelicate, as discussed previously in this chapter.[129] This quadruply-stranded metallohelicate was shown to undergo spontaneous dimerisation to form an interlocked quadruple helicate, in which the interlocked helicate is the thermodynamically stable one and the quadruply stranded helicate is the kinetic product.

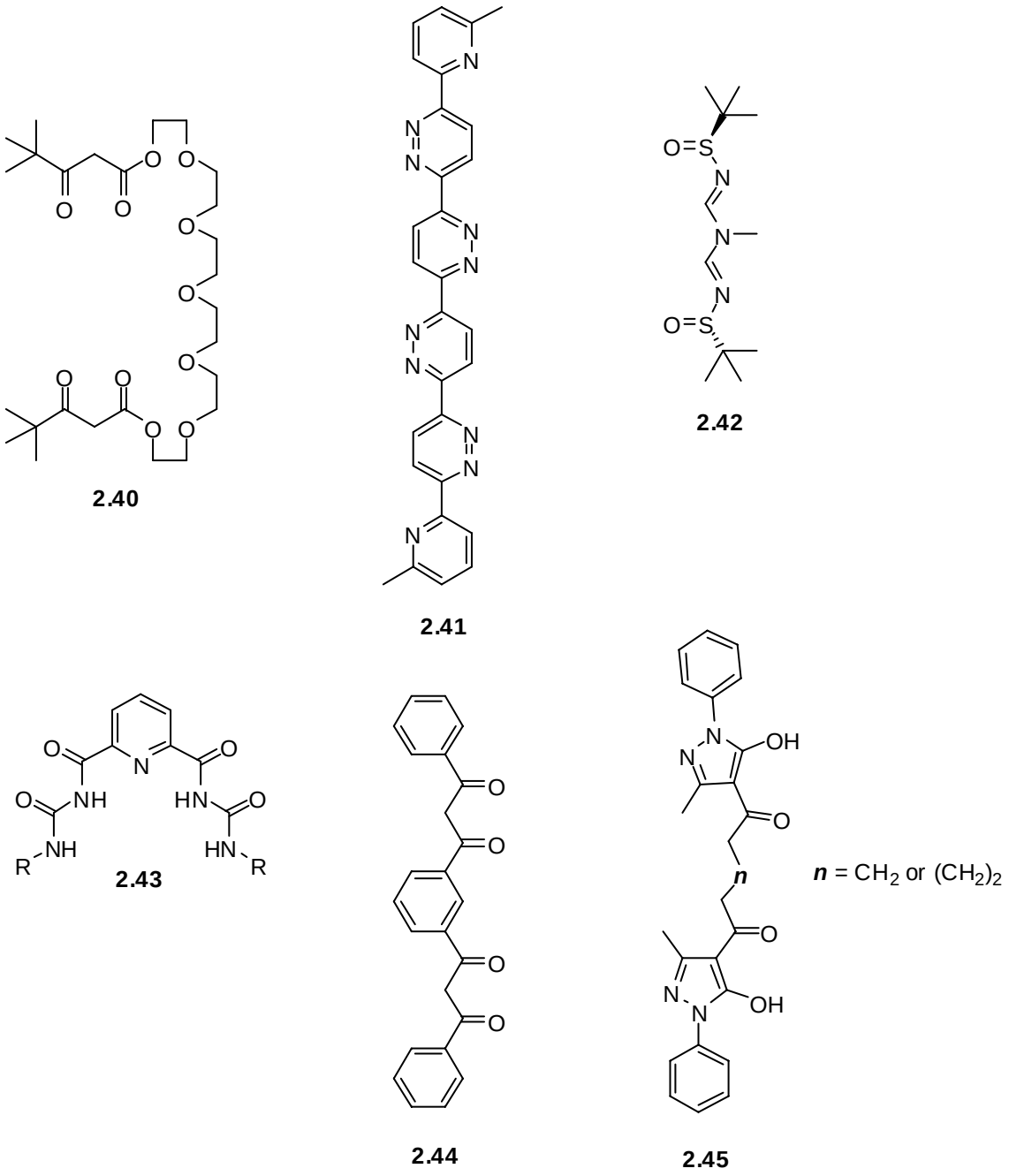


Figure 2.30 – *Examples of ligands reported in the literature to form quadruply-stranded helicates.*

To the best of our knowledge the quadruple helicate discussed in this thesis is the first such example of a dinuclear copper(II) quadruply-stranded helicate having square-pyramidal metal termini. Consequently, this structure is unique and belongs to a very rare group of complexes.

Numerous attempts were undertaken to recrystallise the sample in order to obtain a better refinement; however these proved unsuccessful. Attempts were also made to grow crystals of the quadruple helicate with different solvents and crystallisation techniques. However, most of these experiments gave insoluble precipitates or very fine crystalline solids that were not suitable for X-ray crystallography. In fact in one particular case X-ray analysis revealed a completely different copper complex, as discussed in the previous section (**2.38**). Fortunately, crystals of the same quadruply-stranded helicate complex were able to be grown from a different solvent system of copper nitrate dissolved in methanol and ligand **2.19** dissolved in chloroform. Crystals suitable for X-ray analysis were obtained and are discussed in the next section in more detail.

*Another crystal structure of the complex with $Cu(NO_3)_2$ (**2.39b**)*

Blue crystals of the quadruple helicate grown from different solvents were found to be suitable for X-ray crystallography. Unfortunately, these crystals were also air sensitive and began to crack and decompose once out of the solvent mixture. Luckily these crystals proved to be more stable in the oil than **2.39a** and there was therefore more time to select and mount a decent crystal under the cold nitrogen stream before they began to decompose. The thin crystals were poor diffractors and found to all be highly twinned again. Once again there was a lot of disorder in the nitrate anions and solvent molecules. Therefore the crystallography routine "*Squeeze*"[158] was used to remove additional electron density from the disordered nitrate anions and disordered solvent molecules. Removal of this disorder through the "*Squeeze*"[158] routine reduced the R_1 value to 7.18%.

The structure solved in the same monoclinic space group C2/c with the same cell as **2.39a**. There are two nitrogen bound half ligands, one whole ligand molecule and a water molecule coordinated to the copper atom in the asymmetric unit. The asymmetric unit is depicted in figure 2.31, with the oxygen of the water molecule still shown and the hydrogens removed for clarity. The two halves of the molecule are related by a two-fold rotation axis that passes through the two central quaternary carbon atoms of the two half ligand molecules.

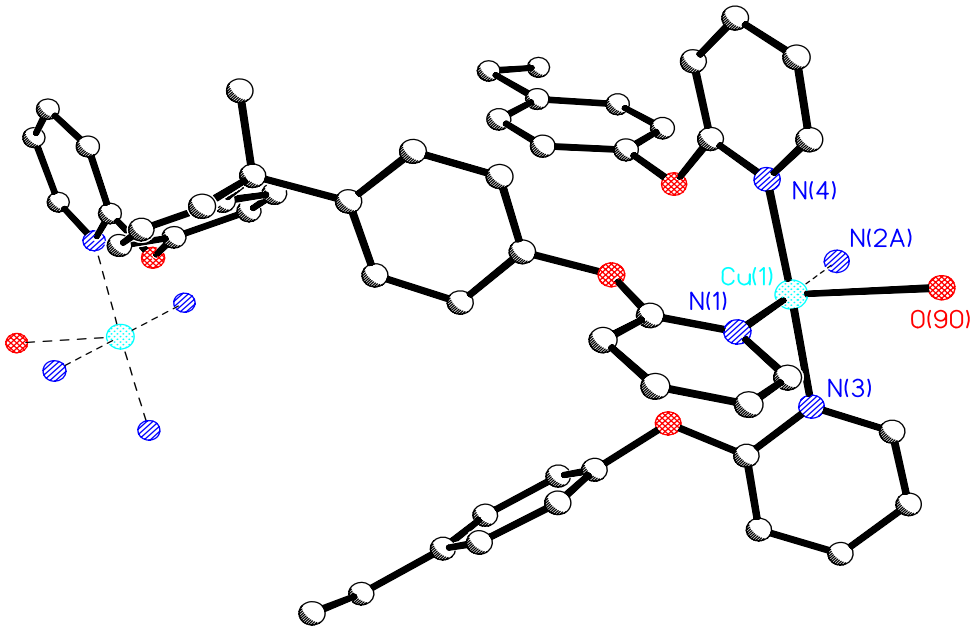


Figure 2.31 – *Contents of the asymmetric unit of* ***2.39b****. Selected bond lengths (Å) and bond angles (°): Cu1-N1 2.018(3), Cu1-N2A 2.022(3), Cu1-N3 2.036(3), Cu-N4 2.037(3), Cu1-O90 2.426(3), N1-Cu1-N2A 177.6(1), N1-Cu1-N3 90.0(1), N1-Cu1-N4 90.98(1), N2-Cu1-N3 89.4(1), N2-Cu1-N4 89.6(1), N3-Cu1-N4 177.7(1), N1-Cu1-O90 91.1(1), N2A-Cu1-O90 91.3(1), N3-Cu1-O90 90.6(1), N4-Cu1-O90 91.4(1).*

Complex **2.39b** is very similar to complex **2.39a**. A picture of the quadruply-stranded helicate using the ORTEP X-ray drawing program is depicted in figure 2.32. The copper atoms in **2.39b** have an identical square-pyramidal geometry to that seen in **2.39a**, binding to nitrogens of four separate ligands and a water molecule. Once again the four nitrogens lie on the basal plane and the apical position is occupied by the water molecule. The water molecule coordinates to the copper atom through the oxygen atom with a Cu-O bond length of 2.426Å. The four Cu-N bond lengths are also very similar to that seen previously in complex **2.39a** and range between 2.018Å and 2.036Å. The distance between copper atoms in a cage is 13.244Å and the distance between the central quaternary carbon atoms of opposing ligands is 10.679Å (C1-C1A) and 10.841Å (C70-C50). Once again this is similar to the previously discussed crystal structure. The benzene rings twist about the central quaternary carbons of the ligand strands and the pyridine rings are approximately perpendicular to the planes of the attached benzene rings, which allow the pyridine rings to wrap around the copper atoms in a helical fashion.

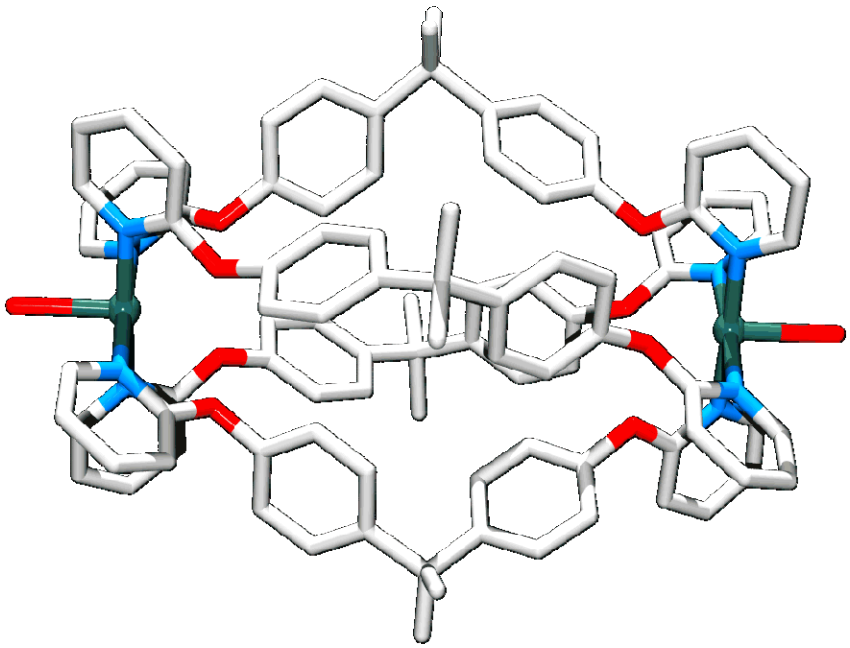


Figure 2.32 – *View of the quadruply-stranded helicate using the ORTEP X-ray drawing program.*

Complex **2.39b** exhibits approximate D_4 symmetry. The space group is centrosymmetric C2/c, therefore mirror image molecules with the opposite twist are present in the crystal structure. Complex **2.39b** is an unsaturated homostranded homotopic quadruple helicate, as defined previously.

In 1998, Barbour and co-workers reported a related dinuclear quadruply-stranded copper complex.[159] The crystal structure revealed a molecular cage in which the two octahedral copper atoms are bound to four bridging ligands in the equatorial positions and two water molecules in the axial positions, as shown in figure 2.33. However, the ligand strands were arranged in a linear fashion around the copper centers to give a M_2L_4 molecule cage-like complex as opposed to a helical cage like **2.39**.

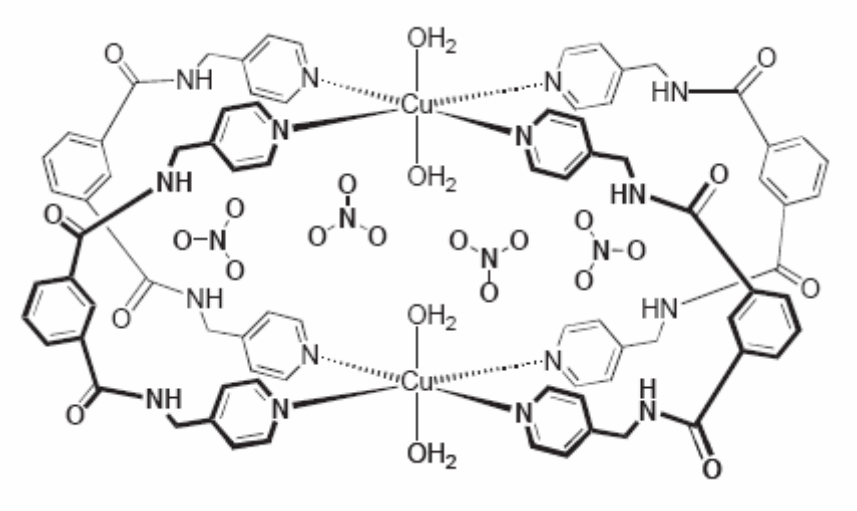
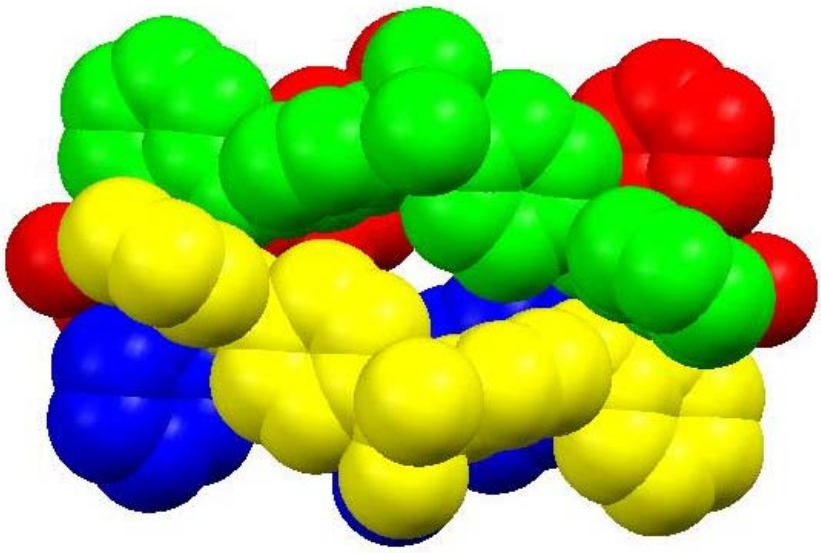
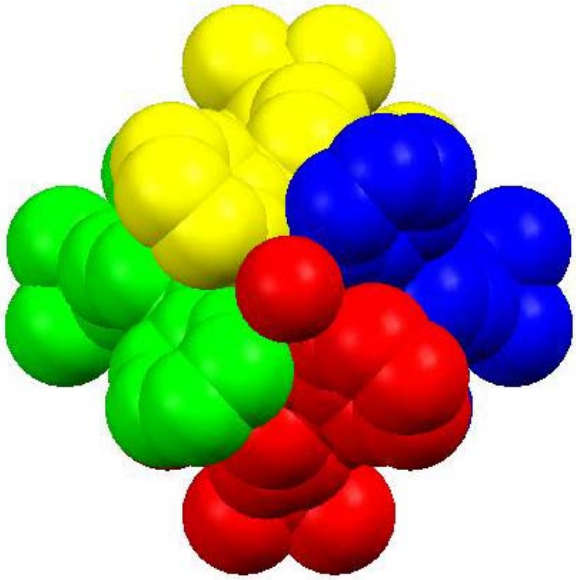


Figure 2.33 – *Illustration of the dinuclear quadruply-stranded copper complex synthesised by Barbour and co-workers with the ligand strands arranged in a linear manner around the copper atoms.*

Like the other structure there is a small void inside the cavity of the helicate with a volume of 45.9 $Å^3$. Unfortunately the squeeze program removed any residual electron density from the structure and therefore there is now no nitrate counterions, solvent molecules and water molecules in the model of the structure. A space-filling diagram shows the small void located in the central cavity of the quadruple helicate, in figure 2.34(a), with the hydrogens removed for clarity. Each of the ligand strands is a different colour in order to accentuate the helical twist of the quadruply-stranded helicate. The helical pitch of **2.39b** is also clearly seen here and defined by the approximate 90° angle of each ligand with respect to each other around the helical axis. There is also a view of the helicate when looking down the c-axis through the copper atoms, shown in figure 2.34(b). If one looks down through the copper atoms, i.e. an end on view, the molecular structure looks like a propeller blade-type conformation, due to the twisting of the ligand strands about the helical axis.



(a)



(b)

Figure 2.34 – ***(a)*** *Space-filling diagram of the quadruply-stranded helicate, with the four ligand strands in different colours to emphasise the helical twist of the complex.* ***(b)*** *View when looking down the c-axis through the copper atoms.*

The quadruple helicate molecules stack into linear arrays with the Cu-Cu axis parallel to the c-axis. Adjacent linear arrays of helicate molecules are offset from one another by approximately half a structural unit. This almost staggered type arrangement allows the

formation of cavities between helicate cages within an array. However these cavities are not large and are filled by copper coordinated water molecules of two neighbouring helicate molecules within a linear array. The quadruple helicates pack with numerous interactions and short contacts between molecules, such as edge-to-face π interactions between benzene rings and pyridine rings (2.808Å).

*Crystal structure of the complex with $AgPF_6$ (**2.40**)*

A solution of ligand **2.19** was dissolved in chloroform and carefully layered upon a solution of silver hexafluorophosphate dissolved in acetone. Vapour diffusion of ether into the resulting reaction mixture and slow evaporation over time furnished block-like crystals suitable for X-ray analysis. The silver hexafluorophosphate complex crystallises in the centrosymmetric triclinic space group P-1 and forms an interesting dimeric M_2L_2 metallomacrocycle. The asymmetric unit contains one ligand molecule, one silver atom, one non-coordinated hexafluorophosphate anion and an acetone solvent molecule. The discrete structure is shown in figure 2.35 with the hydrogens and solvent molecule removed for clarity.

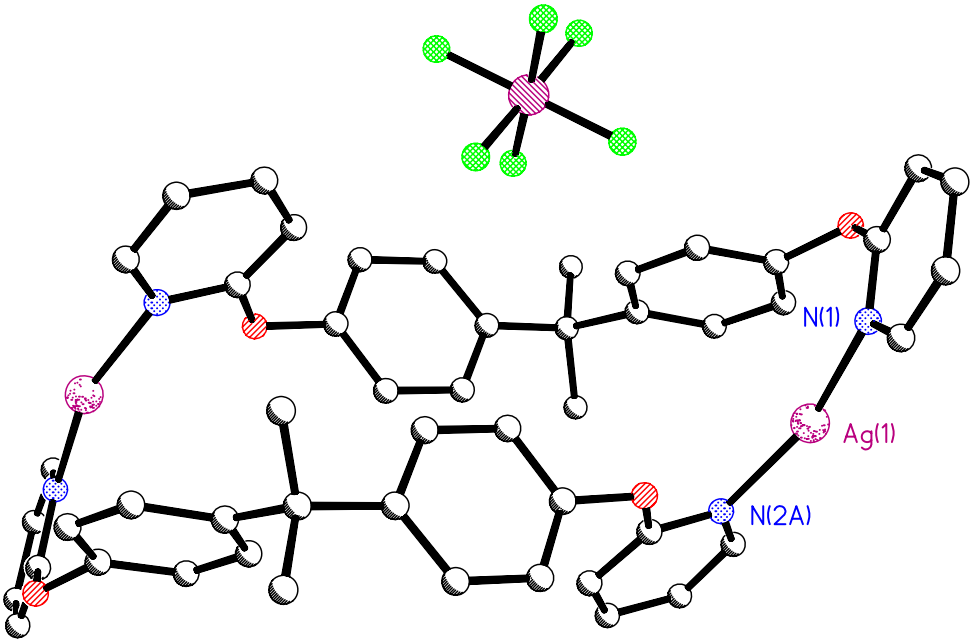


Figure 2.35 - *View of the [2+2] macrocycle **2.40**. Selected bond lengths (Å) and bond angles (°): Ag1-N1 2.190(2), Ag1-N2A 2.181(2), N2A-Ag1-N1 161.48(7).*

The benzene rings of a ligand are almost orthogonal to each other with the pyridine binding arms facing outwards to bond to the silver atoms. The pyridine rings are almost perpendicular to the attached benzene ring, as seen previously in the crystal structure of ligand **2.19** itself and other complexes so far in this thesis.

Two asymmetric units about a centre of inversion combine to give a [2+2] macrocycle, as depicted in figure 2.35, with a Ag-Ag separation of 11.430Å. Each silver atom is coordinated to two pyridine nitrogens with a near linear geometry of 161.48°. This deviation from linearity is quite common in many silver metallosupramolecualar complexes. The silver-pyridine bond lengths of 2.190Å and 2.181Å are similar to related two-coordinate silver(I) complexes.[101, 102, 160-163] The [2+2] macrocycle has a distorted square shaped appearance with two of the sides containing the coordinated silver atoms and the corners comprised of pyridine rings and the quaternary carbons of the Bisphenol A backbone. As a result of the linear connecting silver atoms and the conformation of the ligand the structure looks more like a distorted parallelogram. In typical M_2L_2 rectangular complexes the metal atom forms part of the short side of the rectangle to give its height and the ligands usually make up the length of the rectangle with a 90° angle from the 2-substituted pyridine ring. However, complex **2.40** has the metal atoms forming part of the long side of the rectangle with the four corners formed by the 2-substituted pyridine ring and the quaternary carbon of the propane group. A perspective view of the [2+2] macrocycle illustrating this type of topology is in figure 2.36. This view also shows how the complex has more of a parallelogram shape as opposed to rectangular.

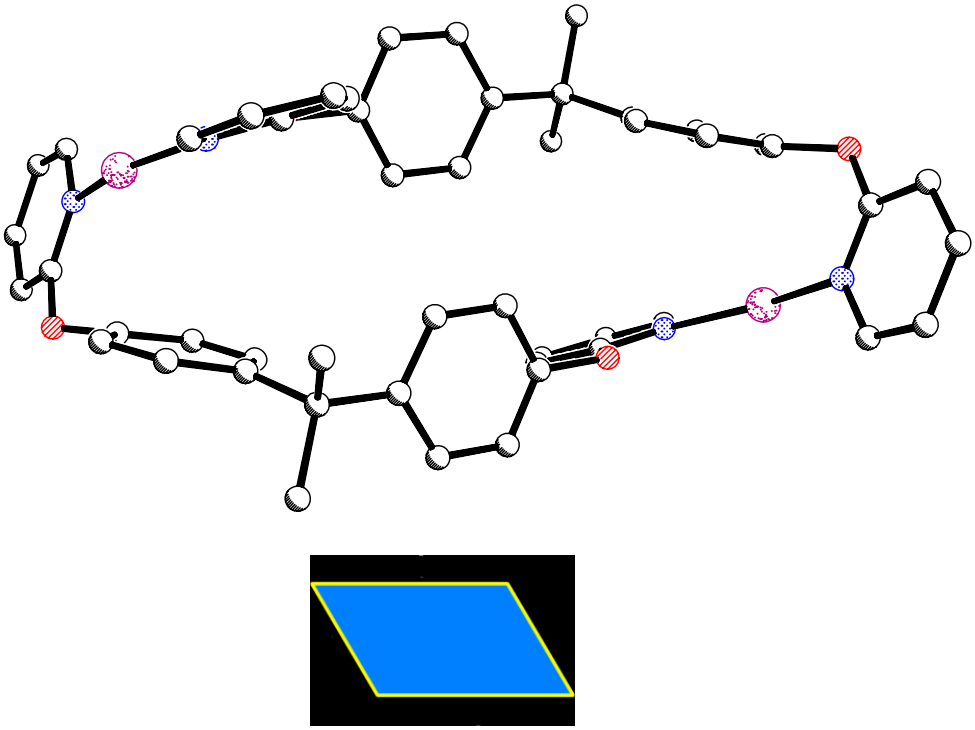


Figure 2.36 – *Perspective view illustrating the parallelogram shape of the [2+2] macrocycle. The hydrogen atoms, hexafluorophosphate anion and acetone solvent molecule are omitted for clarity. A picture of a parallelogram is also illustrated for comparison.*

There are no intramolecular π-π stacking interactions between the benzene and pyridine cores within the macrocycle due to the conformation and overall orientation of the ligands. This is because the two central benzene rings are parallel and significantly off-set from one another, as can be clearly seen in figure 2.36. The benzene and pyridine cores are seen to align with each other on each side of the coplanar benzene rings, with a distance too long for π-π stacking interactions to occur (4.459Å). The absence of π-π stacking interactions within a [2+2] macrocycle is unusual, because such interactions are thought to stabilise such M_2L_2 dimetallomacrocycles.[164]

The [2+2] dimers pack into one-dimensional polymeric chains through edge-to-face π interactions between benzene and pyridine rings of adjacent macrocycles (2.676Å). There are also numerous short intermolecular contacts between the non-coordinating acetone molecules and non-coordinating hexafluorophosphate anions that fill the voids around the dimers and link dimeric chains together into a two-dimensional network.

*Crystal structure of the complex with $AgCF_3SO_3$ (**2.41**)*

A solution of ligand **2.19** in chloroform was added to a solution of silver trifluoromethanesulfonate in acetone. Ether was diffused into the reaction mixture and the solution was left to crystallise in the fridge. Thin needle-like colourless crystals formed on the bottom of the vial after a week. Unfortunately, under the microscope the crystals were found to be brittle thin needles that shattered on contact. Furthermore, once a suitable crystal was finally mounted without breaking and put on the diffractometer, it was found to be highly twinned and had to be taken off. It took several attempts and multiple crystals to finally mount a crystal suitable for X-ray crystallography, although the data collected still showed considerable twinning in the crystal. Consequently, the best data collection resulted in an R_1 value of 7.11%. Attempts to re-grow better quality crystals were unsuccessful.

The silver complex crystallises in the monoclinic space group Cc forming another [2+2] metallomacrocycle, with a different counter anion to complex **2.40**. The asymmetric unit contains two ligand molecules that are bridged by two silver atoms, which are each coordinated to a triflate anion. The rectangular [2+2] macrocycle is shown figure 2.37 with the hydrogen atoms removed for clarity.

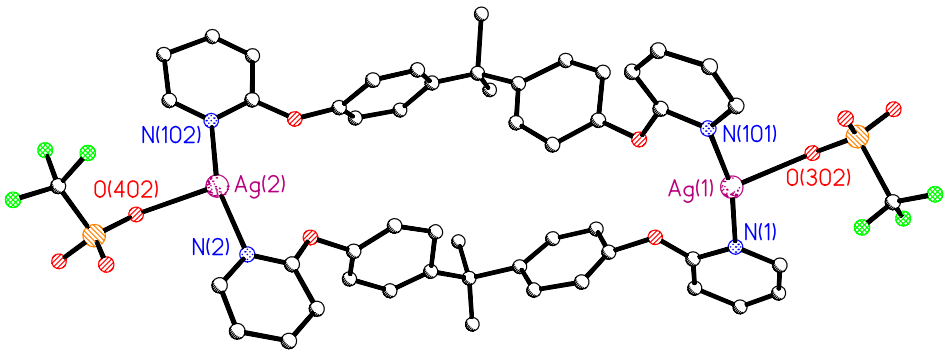


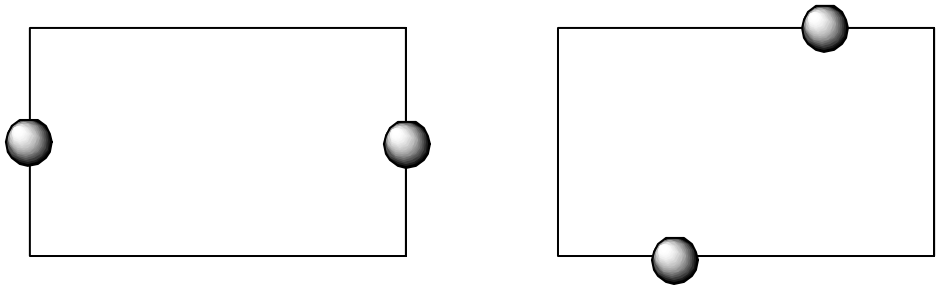
Figure 2.37 – *View of the asymmetric unit of complex **2.41**. Selected bond lengths (Å) and bond angles (°): Ag1-N1 2.23(3), Ag1-N101 2.14(3), Ag1-O302 2.56(3), Ag2-N2 2.19(3), Ag2-N102 2.14(3), Ag2-O402 2.57(2), N101-Ag1-N1 166.1(1), N101-Ag1-O302 103.7(1), N1-Ag1-O302 87.8(1), N102-Ag2-N2 162.7(1), N102-Ag2-O402 87.0(8), N2-Ag2-O402 104.5(9).*

In the crystal structure of **2.41** the benzene rings of each ligand are again slightly twisted away from the mean plane of each other and the binding pyridine rings of each ligand are perpendicular to the attached benzene ring. The orientations of ligands in this complex have been seen previously in the silver hexafluorophosphate [2+2] macrocycle (**2.40**).

Both silver atoms bind to two pyridine nitrogens and one triflate anion. The coordination geometry of the silver atoms can therefore be described as a 'T-shaped' geometry with a small deviation from linearity due to the strong interaction with the triflate anion. The silver-oxygen donor bond lengths fall within the range accepted for other similar compounds.

Complex **2.41** has a typical rectangular shape comprised of metal atoms that form the short sides of the rectangle to give its height and the ligands that make up the length. The corners of the rectangle are provided by the four 2-substituted pyridine rings. The distance between silver atoms is 13.729Å, which is a much larger separation in comparison to the other silver [2+2] macrocycle synthesised with the same ligand. The height of the rectangle is 5.938Å (C1-C101), which was measured from the two central carbons of the bisphenol A backbone of the long sides of the rectangle.

Two similar but also quite different [2+2] macrocycles (**2.40** and **2.41**) were synthesised from ligand **2.19**. The two complexes were found to be very similar in topology, but quite different in shape. Both reactions resulted in the formation of [2+2] rectangular macrocycles with different silver salts. Complex **2.40** has a parallelogram shape with $AgPF_6$, in which the metal atoms formed as part of the long side of the rectangle and the corners were formed by the 2-substituted pyridine ring and the central carbon of bisphenol A backbone. In comparison, complex **2.41** has a more typical M_2L_2 rectangular box shape, in which the short sides are made up of the metal atoms. Figure 2.38 schematically illustrates more clearly these two M_2L_2 rectangular topologies.



(a) (b)

Figure 2.38 – *Schematic illustration of two M_2L_2 macrocyclic topologies.* ***(a)*** *M_2L_2 complex with the metal atoms forming the short sides of the rectangle.****(b)*** *M_2L_2 complex with the metal atoms forming as part of the long side of the rectangle.*

The packing seen in the triflate complex is similar to that seen in the hexafluorophosphate complex. Once again there are no intramolecular π-π stacking interactions between the benzene and pyridine cores within a macrocycle, because the rings on each side of the rectangular complex are co-planar and significantly off-set from one another. However, there are multiple edge-to-face π interactions between benzene rings and pyridine rings of adjacent macrocycles linking the macrocycles together into a three-dimensional structure. In this case the benzene rings are oriented edge on to the facially arranged pyridine rings. There are also weaker edge-to-face π interactions between the binding pyridine arms of adjacent molecules. The three-dimensional network is also linked by some hydrogen bonding interactions between triflate oxygens and fluorides with ligand hydrogens. The oxygens of the triflate anions have hydrogen bonding interactions with pyridine hydrogens (2.467Å and 2.567Å), benzene hydrogens (2.351-2.698Å) and hydrogens from the methyl groups (2.495-2.672Å) of the bisphenol A backbone. There is also an interaction between the triflate fluorines and the hydrogens of the ligands (2.651Å).

Over the years, similar silver M_2L_2 rectangular macrocyclic structures to the two described above have been synthesised by various members of the Steel group. Hartshorn et al. made [2+2] metallomacrocycles from ligands 1,4-bis(2-pyridyloxy)benzene[101] and 1,3-bis(2-pyridyloxy)benzene[102] with $AgNO_3$. These two macrocycles display similar distorted T-shaped geometries around the silver atoms through coordination to two 2-substituted pyridines and a water oxygen atom. What is interesting about these structures is the strong π-π stacking interactions within a

macrocycle between the two central benzene rings that potentially stabilize and encourage the formation of the M_2L_2 dimer. The [2+2] macrocycles also have a rectangular shape, like that schematically depicted in figure 2.55(a) in which the short sides of the rectangle are made up of the metal atoms. The two complexes made by Hartshorn et al. are similar to complex **2.41** by means of a similar M_2L_2 rectangular topology. Hartshorn et al. also synthesised a very similar [2+2] silver macrocycle to complex **2.41** with ligand 1,4-bis(2-pyridylsulfanylmethyl)benzene and $AgNO_3$.[165] This macrocycle exhibited no intramolecular π-π stacking interactions between central benzene rings, because they were significantly off-set from one another and had a similar rectangular topology to complex **2.41** with the silver atoms on the short sides of the rectangle. By replacing the central benzene sub-unit with a naphthalene unit O'Keefe et al. synthesised a [2+2] silver macrocycle from 2,6-bis(2-pyridyloxy)naphthalene and $AgNO_3$.[163] This macrocycle exhibited the same rectangular topology with silver atoms as the short sides of the rectangle and was also stabilized by internal π-π stacking interactions between central naphthalene cores. Numerous other M_2L_2 silver macrocycles exhibiting a similar rectangular shape with the metal atoms on the short sides have been reported in the literature.

In comparison, Fitchett et al. synthesised a M_2L_2 macrocycle similar to complex **2.40** from ligand 1,2-bis(3-pyridylmethoxy)benzene and $ZnBr_2$.[107] The silver macrocycle **2.40** has the same rectangular appearance to the zinc macrocycle with the metal atoms connecting the two ligands along the long sides of the rectangle, as depicted schematically in figure 2.38(b).

*Crystal structure of the complex with $ZnBr_2$ (**2.42**)*

A methanol solution of zinc bromide was layered upon a dichloromethane solution of ligand **2.19**. Slow evaporation of this solution produced colourless thin crystals that were suitable for X-ray crystallography. The complex crystallised in the monoclinic space group $P2_1/n$ to give a one-dimensional helical coordination polymer. The asymmetric unit contains one ligand molecule, one metal atom, two disordered bromide counterions and a partially occupied methanol solvent molecule. A section of the helical polymer is shown in figure 2.39 to clearly show the connectivity of the atoms with the hydrogens and solvent molecules omitted for clarity. The bromine atoms are disordered

over two sites, with the major contributing bromine atoms 90% occupied and the methanol molecule has only 50% occupancy.

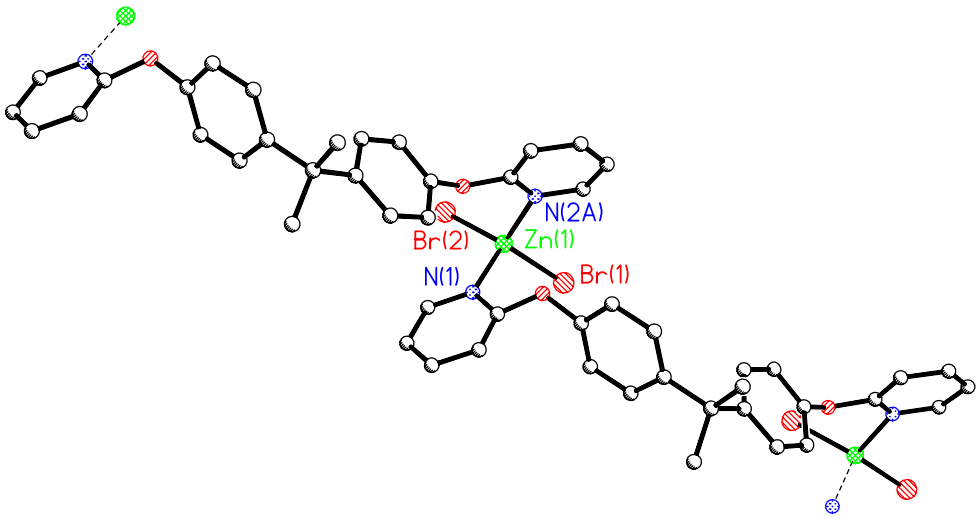


Figure 2.39 - *A section of the one-dimensional helical coordination polymer* ***2.42****. The minor 10% component of the disordered bromine atoms is not shown. Selected bond lengths (Å) and angles (°): Zn1-N1 2.078(4), Zn1-N2A 2.066(4), Zn1-Br1 2.407(1), Zn1-Br2 2.366(1), N2A-Zn1-N1 103.2(2), N1-Zn1-Br1 106.8(1), N2A-Zn1-Br1 107.4(1), N1-Zn1-Br2 107.1(1), N2A-Zn1-Br2 113.7(2), Br2-Zn1-Br1 117.43(7).*

The zinc atom coordinates to two pyridine nitrogens and two bromine atoms with a distorted tetrahedral geometry. The observed distorted deviation from tetrahedral is accentuated by the disorder of the two bromine atoms, with the major component having a small deviation between the bromine atoms of 117.4°. In comparison the minor component has a much larger deviation of 125.1° (N1-Zn1-Br1'), which is possibly why it only has 10% occupancy. The Zn-N bond lengths are 2.066Å and 2.078Å and the Zn-Br bond lengths of the major component are 2.366Å and 2.407Å. The Zn-Br bond lengths in the minor component were found to be slightly shorter (2.253Å) and longer (2.623Å) than that of the major component. The pyridine binding arms of the ligand both lie on the same side of the 'V' shaped Bisphenol A backbone and are positioned to point slightly outwards to bind metal atoms. The pyridine binding arms are once again near perpendicular to the attached benzene ring allowing the pyridine rings to wrap around the zinc atoms in a helical fashion.

The helix propagates down the c-axis with repeat units of the helical chain related by translation. The ligand is achiral and the structure crystallises in the centrosymmetric monoclinic space group $P2_1/n$. Thus, the structure must contain both right- (P) and left-handed (M) helices that are related by symmetry. An illustration of the helix is shown in figure 2.40, with the hydrogens and solvent molecules removed for clarity. The twisting of the pyridine rings to wrap around the zinc atoms inducing the helicity is more clearly seen in this diagram. Consequently, the twisting of the pyridine rings and the tetrahedral binding geometry of the zinc atoms combine to give a helical pitch of 12.509Å, which is equal to the length of the c-axis. This pitch is defined by the distance between zinc atoms, as this is the distance traversed by the one ligand and zinc atom to complete a 360° turn along the helical axis.

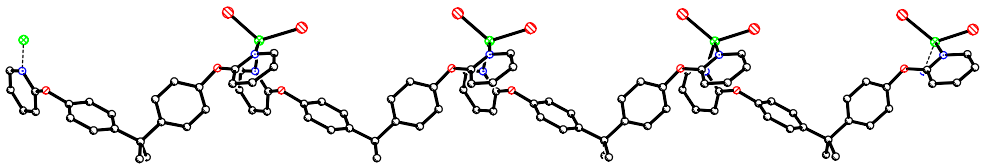


Figure 2.40 – *A perspective view of the one-dimensional helical chain of* ***2.42***.

Packing of the one-dimensional helical chains occurs between the two enantiomers through edge-to-face interactions parallel to the a-axis. Two edge-to-face interactions occur between benzene rings and pyridine rings of ligands with distances of 2.629Å and 2.644Å. There are hydrogen bonding interactions between various hydrogens of the ligand molecules and bromine atoms of adjacent polymer strands within the range 2.964Å-3.029Å. Any spaces in the crystal lattice are filled up by methanol solvate molecules that interact extensively with polymer strands through hydrogen bonds and other short contacts.

*Crystal structure of the complex with $ZnCl_2$ (**2.43**)*

Slow evaporation of a solution containing ligand **2.19** and zinc chloride produced colourless block-like crystals that were suitable for X-ray crystallography. The complex crystallised in the triclinic space group P-1 and revealed a very similar one-dimensional helical coordination polymer to complex **2.42**. In both cases the same solvents were

used to dissolve the ligand and metal salt before layering. In fact, the only difference between the two helical polymers was the use of $ZnCl_2$ as opposed to $ZnBr_2$. The asymmetric unit of complex **2.43** contains one ligand molecule, one $ZnCl_2$ and two methanol solvate molecules, as shown in figure 2.41, with most hydrogens removed for clarity.

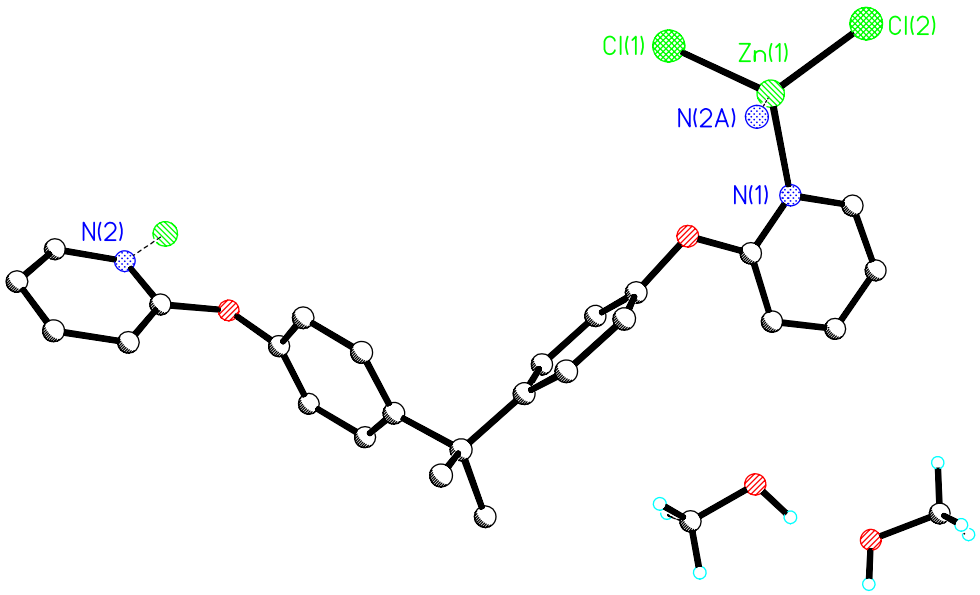


Figure 2.41 – *View of the contents of the asymmetric unit for complex* ***2.43****. Selected bond lengths (Å) and bond angles (°): Zn1-N1 2.058(4), Zn1-N2A 2.059(4), Zn1-Cl1 2.228(2), Zn1-Cl2 2.224(1), N1-Zn1-N2A 100.4(2), N1-Zn1-Cl1 114.4(1), N1-Zn1-Cl2 107.2(1), N2A-Zn1-Cl1 107.5(1), N2A-Zn1-Cl2 116.4(1), Cl2-Zn1-Cl1 110.62(6).*

The zinc atom has a distorted tetrahedral geometry, binding to two chlorine atoms and two pyridine nitrogens of two different ligands. The largest deviation from the tetrahedral geometry is 116.4° (N2A-Zn1-Cl2). The pyridine binding arms of the ligand both lie on the same side of the 'V' shaped Bisphenol A backbone and are positioned to point outwards. The pyridine binding arms are once again near perpendicular to the attached benzene ring allowing the pyridine rings to wrap around the zinc atoms in a helical fashion. The helices have Zn-N bond lengths of 2.058Å and 2.059Å and Zn-Cl bond lengths of 2.224Å and 2.228Å. [166-171]

The one-dimensional chain propagates down the helical axis, with each section of the polymer a translation from the previous. The ligand is once again achiral and the

complex belongs to the centric space group P-1; therefore the structure must contain a mixture of both M- and P-handed helices that are related by a centre of inversion. A depiction of the one-dimensional helical chain is shown in figure 2.42, with the hydrogens and solvent molecules removed for clarity. The helices have a pitch of 12.641Å, which is equal to the length of the c-edge of the unit cell. The pitch distance is between two zinc atoms in the helical chain and is similar in topology to that of the two other helices (**2.36** and **2.42**) mentioned so far in this thesis. What is interesting is this pitch is slightly longer than that of the previous two helical polymers made with the same ligand.

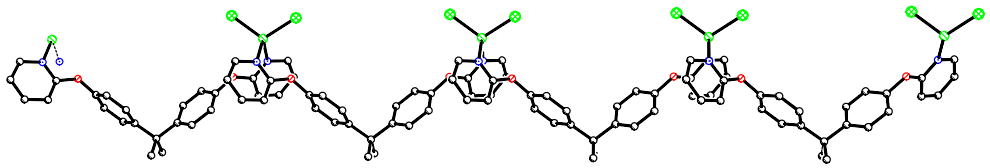


Figure 2.42 – *A perspective view of the one-dimensional helical chain of **2.43**.*

The one-dimensional helical polymer strands pack via edge-to-face interactions between the two enantiomers. Two edge-to-face π interactions occur between benzene rings and pyridine rings of ligands with distances of 2.648Å and 2.797Å that link together the helical strands. There are some C-H···Cl interactions between hydrogens of the ligand and coordinated chlorine atoms. These interactions involve pyridine hydrogens of the ligand molecules and lie in the range 2.837Å-2.869Å. There are also hydrogen bonding interactions between the hydrogens of the methanol solvent molecules and chloride counterions that lie in the range of 2.801Å-2.904Å. Subsequently, any spaces in the crystal lattice are filled by methanol solvate molecules that interact extensively with the polymer strands.

*Other complexes with ligand **2.19***

Ligand **2.19** was reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgCF_3SO_3$, $AgBF_4$, $AgClO_4$, $PdCl_2$, $PdCl_2(PhCN)_2$, $ZnBr_2$ and $ZnCl_2$ under a variety of different conditions. A selection of

these metal salts upon complexation gave X-ray quality crystals with ligand **2.19**, which have already been discussed in detail. Unfortunately, X-ray quality crystals or crystalline solids were not formed with all of these metals. Some of the complexes gave precipitates immediately; however despite several attempts these complexes could not be recrystallised and were not analysed any further. Sometimes instead of complexation, X-ray quality crystals were grown of either the ligand and/or metal salt from the mixed solution.

A crystalline solid was obtained from ligand **2.19** with $Cu(ClO_4)_2$ that was analysed by elemental analysis. The complex analysed with a M_2L_4 stoichiometry suggesting the formation of another quadruple helicate complex. This type of structure is possible, especially since a quadruply-stranded helicate was characterised fully by X-ray analysis with $Cu(NO_3)_2$ already; however there is still the possibility of other assemblies such as a coordination polymer.

No suitable elemental analyses were obtained for full characterization of the quadruple helicate **2.39a** and **2.39b**. The elemental analysis suggests ratios of 1:1 or 2:1 metal to ligand stoichiometries, both of which are not consistent with the structure identified by X-ray crystallography. This suggests that there could be a mixture of products formed. A few of these crystals were used for X-ray analysis, all of which seemed to be M_2L_4 complexes. It was also noted that the crystals were very unstable once removed from the solvent and immediately began to decompose. It is possible the M_2L_4 complex is the most thermodynamically stable and favoured in solution only.

Complexes with ligand 2.21

*Crystal structure of the complex with $CuCl_2$ (**2.44**)*

A copper chloride complex was obtained by layering a methanol solution of cupric chloride upon a dichloromethane solution of the ligand **2.21**. After a week single green plates grew that were suitable for X-ray crystallography. The complex crystallises in the centrosymmetric triclinic space group P-1. The asymmetric unit has one ligand molecule, one metal atom, two chlorine atoms and two methanol solvent molecules. Two asymmetric units about a centre of inversion combine to give a rectangular [2+2]

macrocycle. The crystal structure of complex **2.44** is shown in figure 2.43 with all the hydrogens and solvent molecules removed for clarity.

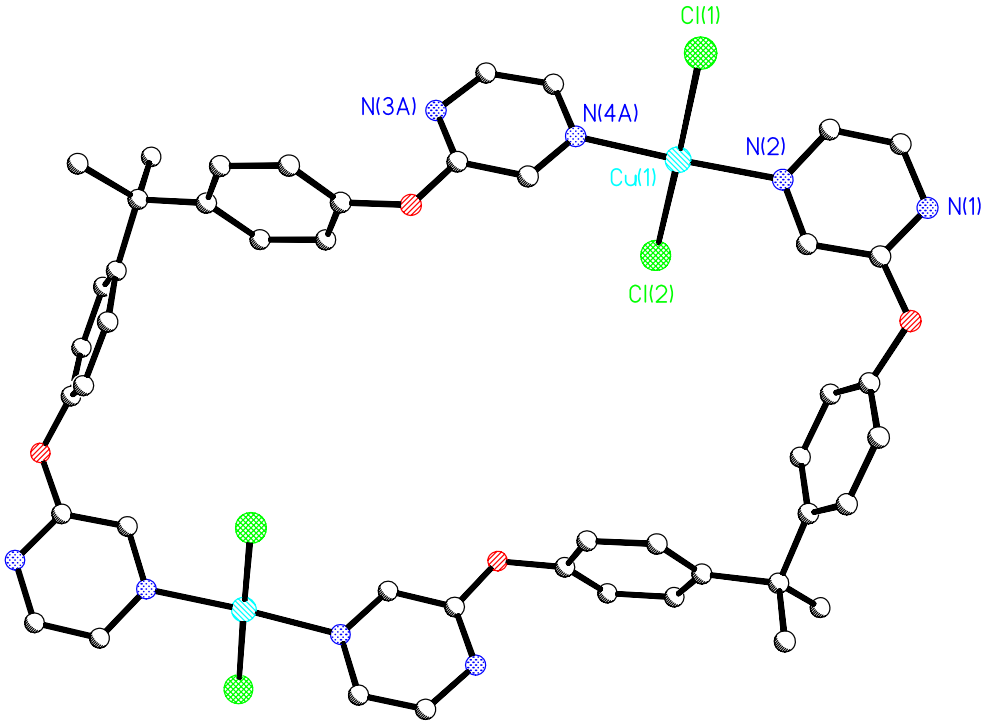


Figure 2.43 - *View of the [2+2] rectangular macrocycle* ***2.44****. Selected bond lengths (Å) and bond angles (°): Cu1-N2 2.040(3), Cu1-N4A 2.031(3), Cu1-Cl1 2.293(1), Cu1-Cl2 2.264(1), N2-Cu1-Cl1 90.1(1), N2-Cu1-Cl2 91.0(1), N4A-Cu1-Cl1 89.1(1), N4A-Cu1-Cl2 89.7(1), Cl2-Cu1-Cl1 177.97(5).*

Each of the copper atoms is 4-coordinate, binding to two pyrazine nitrogens of two separate ligands and two chloride counterions with a square planar geometry. The pyrazine binds to the copper atoms through the less hindered nitrogen, located in the 4-position of the pyrazine ring. Such coordination to the metal atom by the less hindered nitrogen atom is common.[130] The Cu-N bond lengths are 2.031Å and 2.040Å and the Cu-Cl bond lengths are 2.264Å and 2.293Å. The distance between copper atoms across the diagonal of the rectangular macrocycle is 12.471Å. There is a slight twisting about the central quaternary carbon atom on each ligand so that the planes of the benzene rings are not coplanar. The four pyridine rings are almost orthogonal to the planes of their linking benzene rings, with the internal nitrogen atoms being twisted to point outwards and the distal nitrogens pointing downwards, as illustrated in figure 2.43. Overall, the conformation of the ligand in complex **2.44** is similar to that of the ligand

2.21 in the solid state, which has been described previously. The [2+2] macrocycle is rectangular in appearance with copper atoms constructed as part of the long side of the rectangle and the corners formed by two pyrazine rings from separate ligands and the two quaternary carbon atoms of the Bisphenol A backbone. This complex has the same or similar topology to the silver complex **2.40**, which is schematically depicted in figure 2.38(b). The rectangle has a length of 13.354Å, which is the distance between the planes of the two benzene rings across the rectangle. The height of the rectangle is approximately 10.622Å which is the distance across the macrocycle between pyrazine rings. The rectangle does not play host to any guest molecules inside the cavity despite its size. The methanol solvent molecules share the same carbon atom with the oxygen atoms disordered over two sites.

In the packing structure the [2+2] macrocycles are aligned into channels of dimers. There are extensive hydrogen bonding interactions between chloride anions and hydrogens from the ligands. The methanol solvent molecules fill some of the voids in the packing structure, interacting with dimers through hydrogen bonds and other short contacts. There are no other significant interactions.

*Other complexes with ligand **2.21***

Ligand **2.21** was reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgCF_3SO_3$, $AgBF_4$, $AgClO_4$, $PdCl_2$, $PdCl_2(PhCN)_2$, $ZnBr_2$ and $ZnCl_2$. Almost all of these complexes gave immediate precipitates that were unable to be recrystallised and were not analysed further. Consequently, X-ray quality crystals were only grown for one complex, which was discussed above. Some of the more pure precipitates were sent off for elemental analyses, namely the complexes resulting from the reaction of ligand **2.21** with $AgPF_6$, $AgCF_3SO_3$ and $AgClO_4$. These silver complexes all analysed with 1:1 ratios that suggest the formation of discrete complexes, like **2.44**, or more likely coordination polymers.

Complexes with ligands 2.23 and 2.25

Ligands **2.23** and **2.25** were reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgCF_3SO_3$, $AgBF_4$, $AgClO_4$, $PdCl_2$, $PdCl_2(PhCN)_2$, $ZnBr_2$ and $ZnCl_2$. Regrettably, no crystals suitable for X-ray crystallography were obtained with either of the ligands and a lot of insoluble crystalline precipitates were formed. Attempts were made to recrystallise some of the precipitates, however these were unsuccessful and most of the complexes were not analysed any further. Sometimes instead of complexation, X-ray quality crystals were grown for either the ligand and or metal salt straight from the mixed solution.

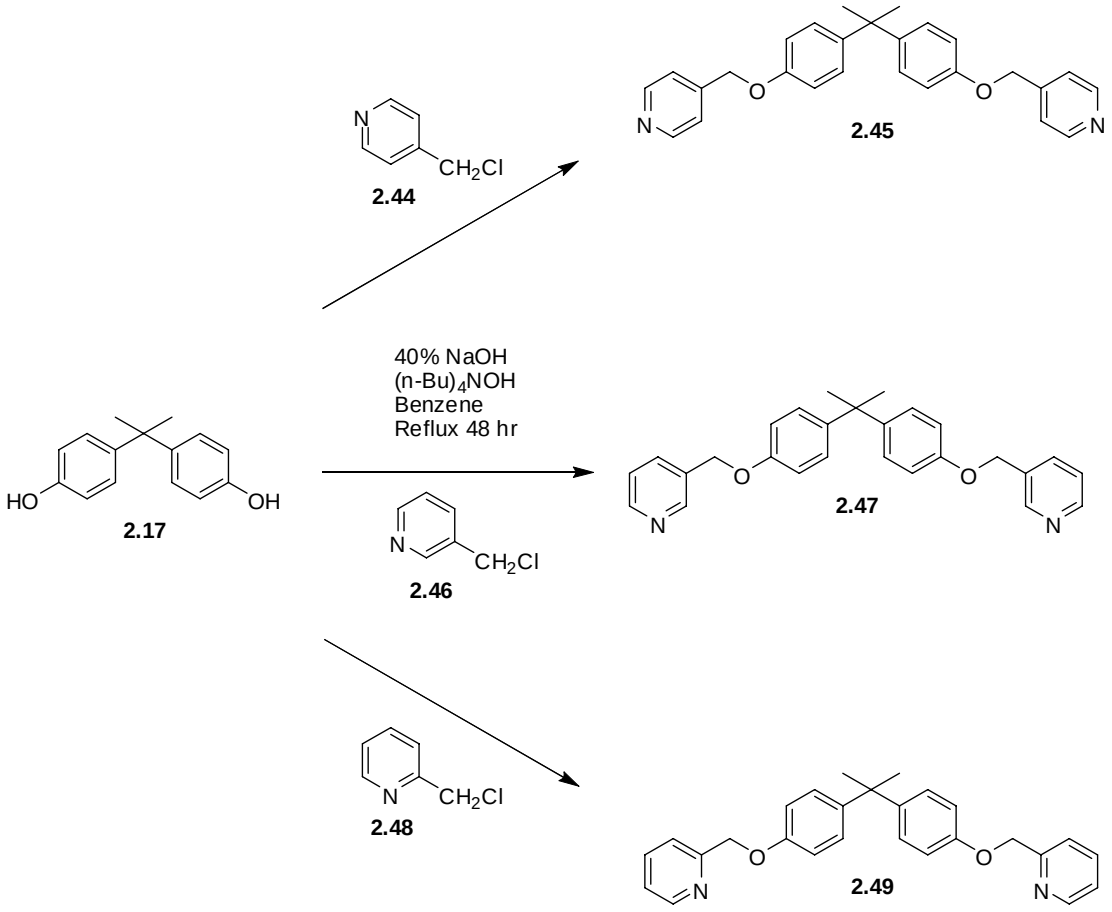
Reaction of ligand **2.23** with $AgPF_6$ and $AgClO_4$ formed colourless crystalline solids that analysed as a 1:1 metal to ligand stoichiometry. This type of 1:1 ratio is quite vague and corresponds to the formation of a polymeric or discrete complex. A white precipitate formed with $AgCF_3SO_3$, which also analysed with a 1:1 ratio.

Elemental analyses were carried out on some of the silver complexes made with ligand **2.25**. Ligand **2.25** was reacted with $AgPF_6$ and $AgCF_3SO_3$ and the products analysed with 1:1 ratios. Again, this could indicate formation of a discrete complex or some kind of polymeric complex. A white precipitate formed immediately on reaction of ligand **2.25** with $AgClO_4$ and analysed with a M_3L_2 stoichiometry. This type of ratio is ambiguous and suggests a more complex coordination mode for the silver atoms. Perhaps there is some sort of cage comprised of silver atoms or coordination of solvent molecules. Unfortunately, no crystals were grown to analyse this further.

Synthesis of the Bisphenol A based -CH_2O- spaced ligands

Another three ligands were synthesised from the Bisphenol A core, this time with a spacer group containing two atoms, instead of just one. The spacer group was extended by use of a methyleneoxy (-CH_2O-) group between the benzene ring and the pyridine ring. These compounds are very similar to ligand **2.19**, but with an extra CH_2 group inserted. Variations on this type of extension have been explored by the Steel group numerous times, with the alteration of the order of atoms in the spacer groups.

The last three ligands synthesised from ligand precursor **2.17** are shown in Scheme 2.3. Ligands **2.45**, **2.47** and **2.49** were synthesised in a method analogous to that of Hartshorn. The reaction conditions adopted have previously been used to synthesise many structurally related ligands.[102, 172]



Scheme 2.3 - *Synthesis of new ligands (**2.45**, **2.47** and **2.49**) based on the Bisphenol A core.*

The new ligands were prepared by a phase-transfer-catalysed (PTC) double alkylation of Bisphenol A (**2.17**) with three isomeric chloromethylpyridines. The three chloromethylpyridines only differ in the position of the nitrogen atom. Ligands **2.45**, **2.47** and **2.49** were synthesised by reacting two equivalents of the appropriate chloromethylpyridine with precursor **2.17** in a solution of benzene, 40% aqueous sodium hydroxide and a few drops of tetrabutylammonium hydroxide. The mixture was then refluxed for 48 hours. Recrystallisation of the crude ligands from petroleum ether/ethyl acetate gave clean yellow or white solids. Ligand **2.45** was isolated in 39%

yield and ligands **2.47** and **2.49** were isolated in 53% and 26% yields. Subsequently, these ligands were fully characterised by elemental analyses, mass spectrometry, melting points and by ^{1}H and ^{13}C NMR.[113]

The extension of these ligands to two-atom spacer groups could potentially allow the ligands to have quite different conformations compared to the previously mentioned flexible ligands, containing only single oxygen-atom spacer groups. Therefore it is advantageous to grow crystals of these ligands in order to investigate their conformations in the solid state. Consequently, crystals suitable for X-ray crystallography were grown for ligands **2.45** and **2.47** and the X-ray structures of these was determined in order to further investigate their conformations in the solid state.

Crystal structure of ligand 2,2-di(4-(4-pyridylmethoxy)phenyl)propane, 2.45

Slow evaporation of an acetonitrile solution gave colourless crystals of ligand **2.45** suitable for X-ray crystallography. Ligand **2.45** crystallises in the monoclinic space group C2/c with half of the molecule in the asymmetric unit. The two halves of the molecule are related by a two-fold rotation axis which passes through the central carbon of the propane group. The structure of **2.45** is depicted in figure 2.55, where the hydrogen atoms are omitted for clarity.

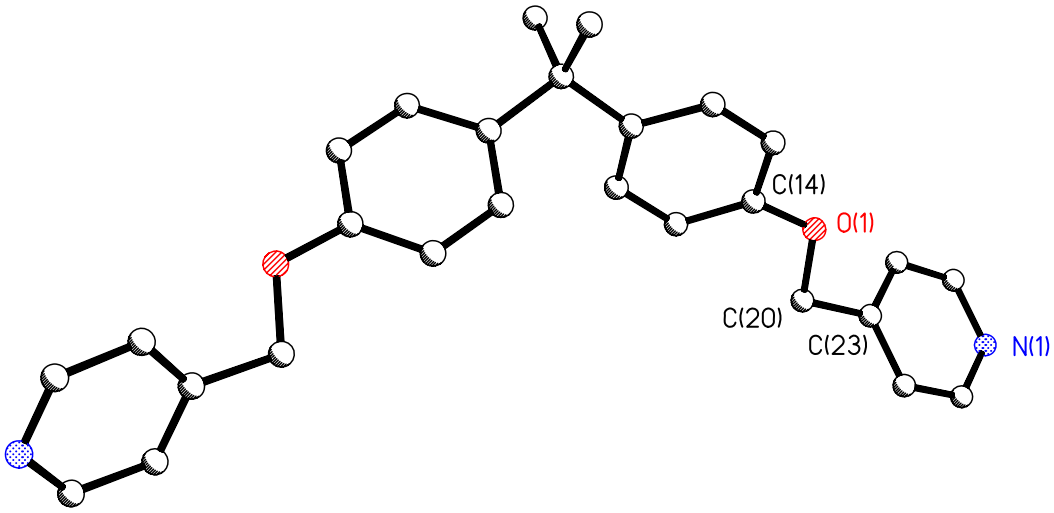


Figure 2.44 – *Crystal structure of ligand* **2.45**. *Selected bond lengths (Å) and bond angles (°): C14-O1 1.381(1), O1-C20 1.431(2), C20-C23 1.506(2), C14-O1-C20 116.94(9), O1-C20-C23 108.2(1).*

In the solid state ligand **2.45** is more symmetrical in conformation than previously mentioned ligands and has a more extended shape. The pyridine rings are facing almost perpendicular to the adjacent benzene rings, with the pyridine nitrogens pointing away. The potential nitrogen donor atoms are separated by a distance of 18.600Å. The symmetrical conformation of the ligand is reflected in the methyleneoxy spacer group adopting an *anti*-periplanar type arrangement, with a C-C-O-C torsional angle of 176.8°.

In the crystal packing, the ligands are aligned into sheets, with hydrogen bonding interactions, C-H···π interactions and edge-to-face interactions. There are C-H···π interactions within a sheet between the hydrogen atoms of the methylene group and the pyridine ring of adjacent ligands (2.509Å). The sheets of ligands are further inter-linked with other sheets of ligands through edge-to-face interactions between the pyridine rings of one sheet and the benzene rings of an adjacent sheet (2.798Å). There are no π-π stacking interactions.

Crystal structure of ligand 2,2-di(4-(3-pyridylmethoxy)phenyl)propane, 2.47

Slow evaporation of a methanolic solution of ligand **2.47** and cadmium nitrate produced nice X-ray quality colourless crystals. Surprisingly, no complex was formed and X-ray crystallography revealed the presence of just ligand **2.47**. Ligand **2.47** crystallises in the triclinic space group P-1 with a full molecule in the asymmetric unit. The structure of **2.47** is depicted in figure 2.45, where the hydrogen atoms are omitted for clarity. Despite the absence of the two-fold rotation, ligand **2.47** has a very similar symmetrical conformation and extended shape to the previously mentioned ligand **2.45** in the solid state. Again the pyridine rings are facing almost perpendicular to the adjacent benzene rings, with the pyridine nitrogens pointing outwards. The positioning of the pyridine nitrogens facing outwards is vital in order to participate in C-H···N intermolecular interactions about a centre of inversion (2.703Å). Also, the two-atom methyleneoxy spacer group adopts a *trans*-periplanar arrangement with C-C-O-C torsional angles of 174.8° and 168.8°. The distance between the two nitrogen donor atoms is 17.528Å, which is only slightly shorter than that for ligand **2.45**.

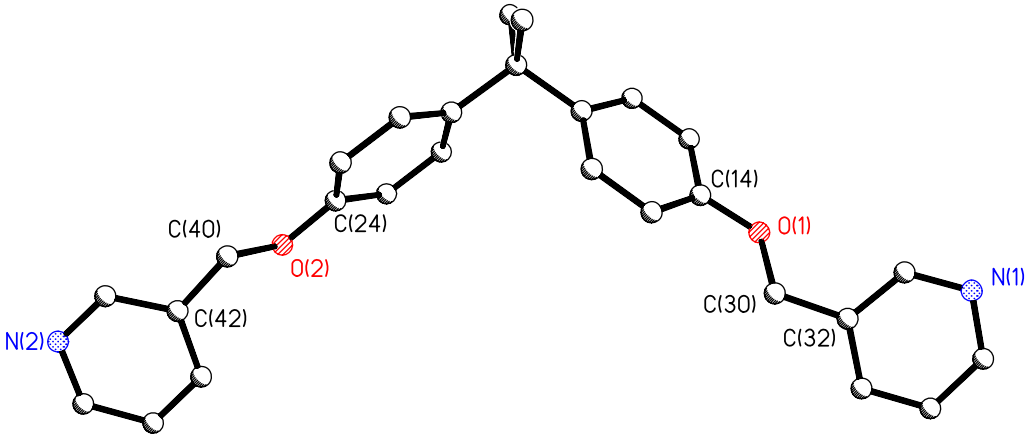


Figure 2.45 - *Crystal structure of ligand* ***2.47****. Selected bond lengths (Å) and bond angles (°): C14-O1 1.384(1), O1-C30 1.437(1), C30-C32 1.510(1), C24-O2 1.386(1), O2-C40 1.437(1), C40-C42 1.507(2), C14-O1-C30 116.97(8), O1-C30-C32 108.62(8), C24-O2-C40 116.08(8), O2-C40-C42 108.92(9).*

In the packing, chains of ligands propagate down the b-axis with molecules interacting with one another through C-H···π interactions. Each ligand molecule has a methylene group (-CH_2-) which interacts with the pyridine ring of adjacent molecules in the chain through C-H···π interactions (2.617Å). The chains of ligands are further inter-linked with other chains of ligands through more C-H···π interactions. There were no observed π-π stacking or edge-to face interactions between molecules.

Ligands **2.45**, **2.47** and **2.49** were reacted with a variety of metal salts under a variety of conditions in order to produce fascinating complexes. Unfortunately, no crystal structures of complexes were obtained with the 4-substituted pyridine ligand **2.45**. Numerous precipitates formed with **2.45** that were insoluble in most solvents and unable to be recrystallised. Some of the complexes were sent away for microanalysis.

Precipitates were obtained from reaction of ligand **2.45** with $CuCl_2$, CuI and $Cu(NO_3)_2$. These complexes all analysed as M_2L compounds. Ligand **2.45** has two nitrogen binding domains; therefore it can only bind a maximum of two metal atoms. Consequently a discrete complex can be formed or a polymer with M_2L units linked by bridging groups or solvents. The CuI complex could have a Cu_2I_2 square motif that bridges ligand strands together into a polymer. CuI squares are a common motif in many complexes.[27]

The reaction of ligand **2.45** with $Cu(ClO_4)_2$ gave a small amount of purple precipitate that analysed as a ML_2 compound. This type of ratio suggests the formation of a discrete dimeric species.

Reaction of ligand **2.45** with $PdCl_2$ gave an orange precipitate immediately that analysed as a 1:1 complex. This could correspond to the formation of a discrete complex or a polymeric array.

Complexes with ligand 2.47

*Crystal structure of the complex with $ZnBr_2$ (**2.50**)*

Zinc bromide dissolved in methanol was mixed with a solution of ligand **2.47** in dichloromethane. Slow evaporation of this solution over time afforded colourless plate-like crystals that were suitable for X-ray crystallography. X-ray analysis of the crystals revealed a unique coordination polymer that solved in the monoclinic space group $P2_1/n$. The asymmetric unit contains one full ligand molecule and one $ZnBr_2$ unit. A section of the one-dimensional coordination polymer, showing its extended connectivity, is shown in figure 2.46, with the hydrogen atoms omitted for clarity.

The ligands of the polymer are severely twisted making the polymer helical. The strands are assembled in a conformation quite different to that of free ligand **2.47**. The benzene rings of the ligand are slightly twisted about the central quaternary carbon atom. One of the ligand's pyridine rings is extended out, almost coplanar with the attached benzene ring, in an *anti* conformation, whereas the other arm of the ligand has a *gauche* conformation. Consequently the conformation of the ligand in complex **2.50** is quite different from that of the free ligand in the solid state. Therefore, the pyridine binding arms of the ligand seem to adopt both *gauche* and *anti* conformations in order to wrap around the zinc atoms in a helical fashion. The zinc atoms are 4-coordinate, binding to two pyridine nitrogens and two bromide counterions. The metal atoms have a distorted tetrahedral geometry with the largest deviation from tetrahedral arising between the bromide counterions with an angle of 120.9°. The Zn-N bond lengths are 2.033Å and 2.041Å, which are within average.[166] The Zn-Br bond lengths of 2.351Å

and 2.365Å are also similar to the previous zinc bromide complex (**2.42**) reported in this thesis.

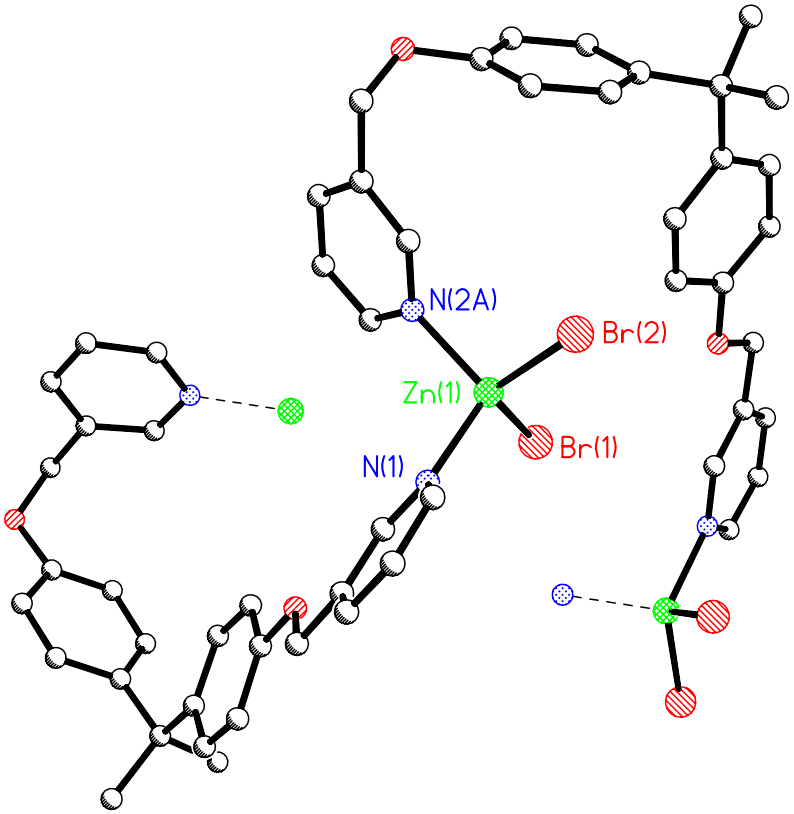


Figure 2.46 – *A section of the one-dimensional polymer strand of* ***2.50****. Selected bond lengths (Å) and bond angles (°): Zn1-N1 2.041(3), Zn1-N2A 2.033(3), Zn1-Br1 2.3655(6), Zn1-Br2 2.3506(6), N2A-Zn1-N1 108.1(1), N1-Zn1-Br1 106.28(9), N1-Zn1-Br2 108.23(9), N2A-Zn1-Br1 105.70(9), N2A-Zn1-Br2 107.2(1), Br2-Zn1-Br1 120.9(2).*

The one-dimensional helical chains propagate down the b-axis of the unit cell along the two-fold screw axis. The complex crystallises in the centrosymmetric space group $P2_1/n$, therefore the structure contains both the left- (M) and right-handed (P) helices that are related by symmetry. A view of the M-helix when viewed looking down the b-axis is illustrated in figure 2.47, with the hydrogens omitted for clarity. The pitch is 8.392Å, which is equal to the length of the b-axis, and is defined by the distance occupied by two ligand molecules and two zinc atoms along the polymer chain. One would expect the pitch distance to be a lot longer than it is for two ligands and two metal atoms. However, due to the helical strands folding on top of one another because of the *gauche* and *anti* conformations of the ligand, the pitch is a lot smaller. The way in

which the helical strands fold up on top of each other makes this helical complex quite different to the other two one-dimensional helical zinc polymers described with ligand **2.19**. The other two zinc one-dimensional helical coordination polymers **2.42** and **2.43** have a more elongated structure due to there being no twisting of the ligand molecules to wrap around the zinc atoms. In comparison, complex **2.50** has ligand/zinc strands that are much more severely twisted and fold up on top of other strands resulting in a more severely twisted helical structure with a shorter pitch distance. The extension of these ligands to two-atom spacer groups has allowed the ligands to have more flexibility to form quite different conformations in the complexes in comparison to the previously mentioned flexible ligands, containing only single oxygen-atom spacer groups.

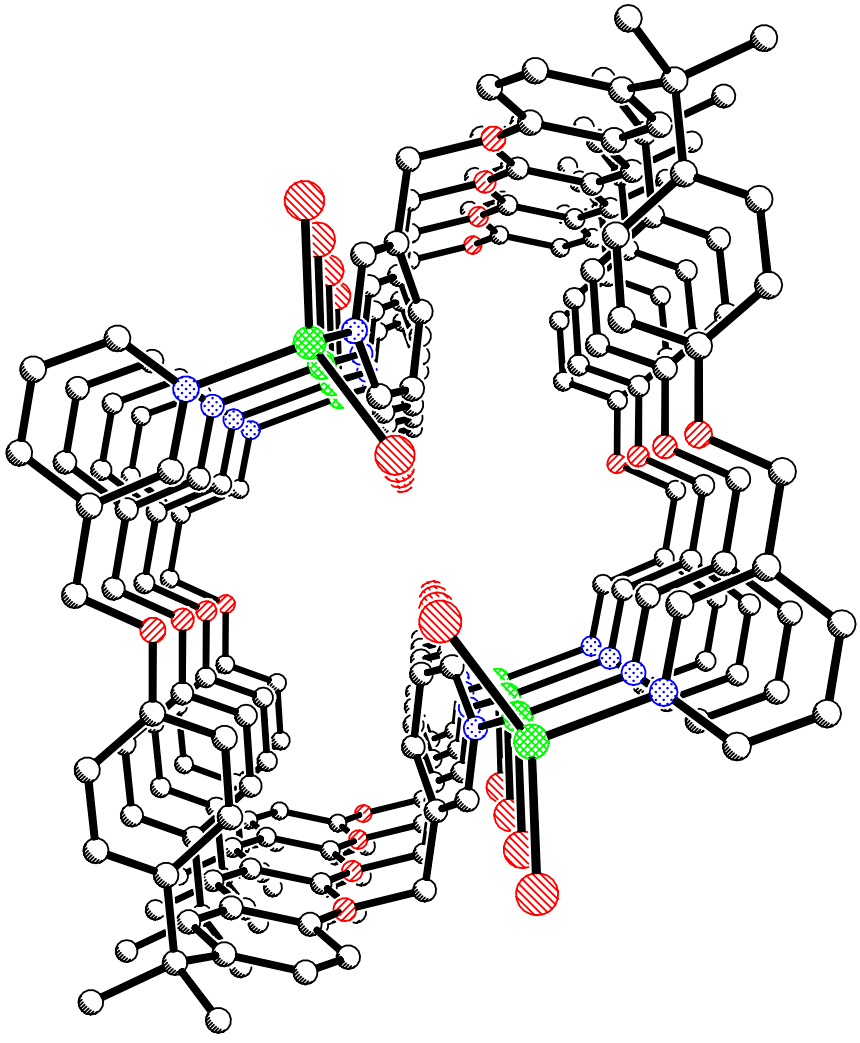


Figure 2.47 – *View of the M-helix strand propagating down the helical b-axis.*

There are grooves in the helices that are big enough to have chains of the opposite chirality slot inside to form an interleaved complex structure. However, due to the conformation of the ligand there are no significant π-π stacking or edge-to-face interactions between opposite chains. In the packing structure there are numerous hydrogen bonding interactions between various hydrogens from the ligand molecules and bromine atoms of attached and adjacent polymer strands. These hydrogen bonding interactions lie within the range 2.874Å-3.043Å.

*Other complexes with ligand **2.47***

Ligand **2.47** was reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $Cd(NO_3)_2$, $AgPF_6$, $AgCF_3SO_3$, $AgBF_4$, $AgClO_4$, $PdCl_2$, $PdCl_2(PhCN)_2$, $ZnBr_2$ and $ZnCl_2$. Regrettably, only one crystal structure of a complex was obtained with ligand **2.47**. Complexation of ligand **2.47** mostly gave precipitates immediately, unfortunately despite several attempts these precipitates could not be recrystallised and were not analysed any further. Sometimes instead of complexation, X-ray quality crystals were grown of either the ligand or metal salt from the complex solution. An example of this was when ligand **2.47** was obtained from a solution with $Cd(NO_3)_2$.

Reaction of ligand **2.47** with copper salts $CuCl_2$, CuI and $Cu(NO_3)_2$ analysed as M_2L compounds. This 2:1 metal to ligand stoichiometry suggests the formation of a discrete complex or a polymer. It is interesting that all three of the copper complexes analyse with the same 2:1 ratio.

Reaction of ligand **2.47** with $PdCl_2$ gave a 1:1 ratio which suggests the formation of a polymeric complex. This structure could be just a linear one-dimensional polymer or perhaps a helical one-dimensional polymer similar to that formed with $ZnBr_2$.

Complexes with ligand 2.49

*Crystal structure of the complex with $Cu(NO_3)_2$ (**2.51**)*

A copper nitrate complex was obtained by layering a methanol solution of copper nitrate over a methanol solution of ligand **2.49**. After slow evaporation of this solution single blue crystals grew on the sides of the vial suitable for X-ray crystallography. The complex crystallises in the triclinic space group P-1. X-ray analysis revealed a 1:1 metal to ligand complex, as shown by the contents of the asymmetric unit, which grows into a one-dimensional coordination polymer. The asymmetric unit contains one whole ligand molecule, two half copper atoms and two coordinated nitrate anions. The contents of the asymmetric unit are shown in figure 2.48, with the hydrogens excluded for clarity.

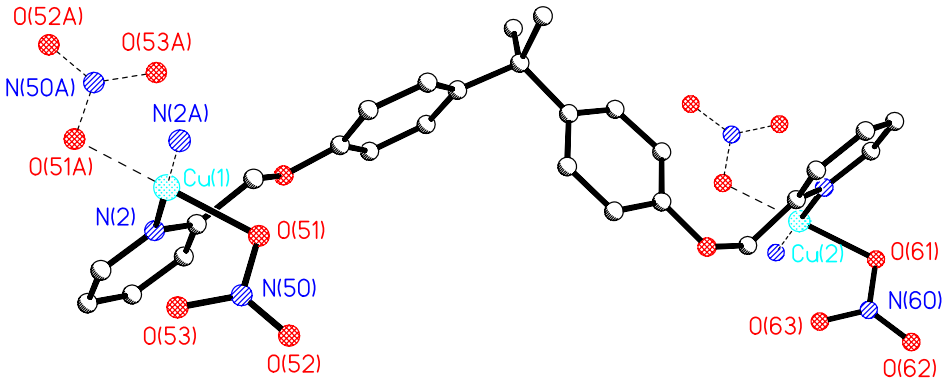


Figure 2.48 – *The asymmetric unit of complex **2.51** showing the 1:1 metal to ligand stoichiometry. Selected bond lengths (Å) and bond angles (°): Cu1-N2 1.984(5), Cu1-O51 2.012(4), Cu2-N1 1.994(5), Cu2-O61 2.001(5), N50-O51 1.304(6), N50-O52 1.216(6), N50-O53 1.232(6), N60-O61 1.303(8), N60-O62 1.219(8), N2-Cu1-N2A 180.0(2), N2-Cu1-O51A 89.0(2), N2-Cu1-O51 91.0(2), N2A-Cu1-O51A 91.0(2), N2A-Cu1-O51 89.0(2), O51-Cu1-O51A 180.0(2), N1-Cu2-N1B 180.0(2), N1-Cu2-O61 88.9(2), N1B-Cu2-O61 91.1(2), N1-Cu2-O61B 91.1(2), N1-Cu2-O61B 88.9(2), O61-Cu2-O61B 180.0(2).*

Each of the copper atoms is four-coordinate square planar, being coordinated by the nitrogen atoms of two separate ligands and two monodentate coordinating nitrate anions. The ligand molecules are each bound to two copper atoms which in turn are coordinated to two monodentate nitrate anions through one of the oxygen atoms. In this complex the pyridine nitrogens of the ligands are *trans* with respect to each other as are the two terminal nitrate anions. The benzene rings of the ligand are twisted away from

each others mean planes about the central quaternary carbon atom. Interestingly, in complex **2.51** both the *gauche* and *anti* conformations of the ligand binding arms are observed. The ligand binding arm that coordinates to Cu1 is extended out in an *anti* conformation, whereas the other arm of the ligand adopts a *gauche* conformation. The pyridine nitrogens are now pointing outwards in opposite directions away from each other.

Cu1 has a Cu-N bond length of 1.984Å (Cu1-N2) and coordinates to the oxygen atom of the nitrate anion with a bond length of 2.012Å (Cu1-O51). There is also a much weaker interaction between Cu1 and another oxygen of the monodentate nitrate anion of 2.479Å (O53), therefore the structure can be considered to be pseudo-octahedral. Cu2 has a Cu-N bond length of 1.994Å (Cu2-N1) and coordinates to the monodentate nitrate anion through the oxygen with a bond length of 2.001Å. Cu2 also has a weaker interaction between the copper atom and the other oxygen of the monodentate nitrate anion of 2.503Å (O63). Overall these bond lengths are similar to 4-coordinate square planar copper(II) complexes reported in the literature.[173-175]

The polymer propagates in one-dimension with the copper atoms on centers of inversion. As a result the polymer chain has a continuous alternating orientation of ligands between the metal atoms, so each copper atom is coordinated to a ligand above and a ligand below. The result is a one-dimensional zig-zag polymer with an alternating ligand orientation, as shown in figure 2.49, which clearly shows the *anti* and *gauche* conformations of the ligand's binding arms.

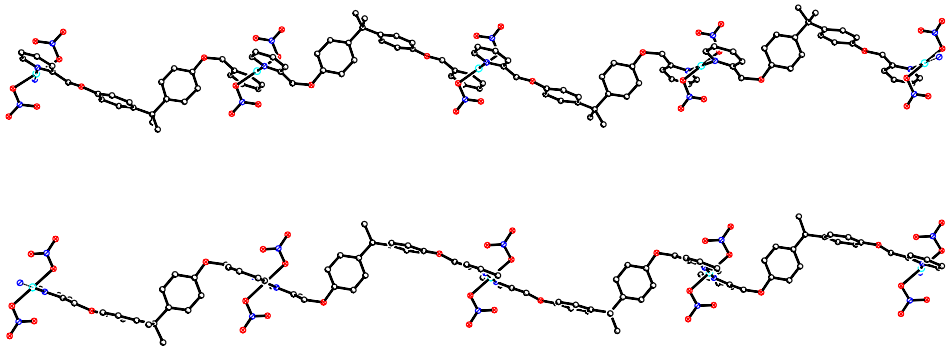


Figure 2.49 – *Two different views showing a section of the one-dimensional coordination polymer* ***2.51****. These diagrams clearly depict both the* anti *and* gauche *conformations of each ligand's arms.*

In the packing of complex **2.51** the one-dimensional polymer strands pack vertically with chains slightly offset from one another. There are C-H···π bonding interactions between the hydrogen atoms of the methyl groups and benzene rings of adjacent polymer strands (2.318Å). The oxygen atoms of the coordinated nitrate counterions are also involved in numerous C-H···O interactions between aromatic hydrogens from ligands on adjacent polymer strands. These distances range between 2.541Å and 2.697Å.

*Other complexes with ligand **2.49***

Ligand **2.49** was reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgCF_3SO_3$, $AgBF_4$, $AgClO_4$, $PdCl_2$, $PdCl_2(PhCN)_2$, $ZnBr_2$ and $ZnCl_2$. Unfortunately only one crystal structure was obtained with ligand **2.49**, which has already been discussed in detail above. Complexation of ligand **2.47** mostly gave precipitates immediately, unfortunately, despite several attempts, these precipitates could not be recrystallised and were not analysed further.

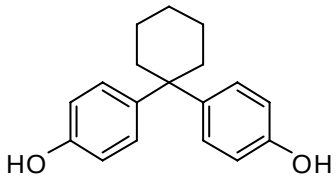
Complexation of ligand **2.49** with CuI produced an orange/yellow crystalline solid after a few months. Elemental analysis indicated a M_2L stoichiometry that suggests the possible formation of a discrete complex, or more likely, another copper coordination polymer similar to **2.51**. CuI often dimerises into Cu_2I_2 squares, which are a common motif in CuI complex structures. Therefore the 2:1 ratio could give a one-dimensional polymer composed of ligands linked to Cu_2I_2 squares units.

Reaction of ligand **2.49** with $PdCl_2$ produced an orange precipitate that analysed with a 1:1 ratio.

Synthesis of the Bisphenol Z based -O- spaced ligands

Another series of two armed bridging flexible ligands were designed and synthesised around a Bisphenol Z backbone. The Bisphenol Z ligand precursor was reacted with the same haloazines and chloromethylpyridines as the Bisphenol A based ligands to create a new range of symmetrical ligands. Bisphenol Z is composed of a central rigid

cyclohexane ring linked to two aromatic benzene rings, as illustrated by ligand precursor **2.52** in figure 2.50. This construction has a very similar 'V-type' arrangement to that of the Bisphenol A ligands, with the two aromatic benzene groups acting as the arms of the 'V' linked via the central quaternary carbon atom. 4,4'-Cyclohexylidenebisphenol, commercially known as Bisphenol Z, is not used commercially as much as Bisphenol A.



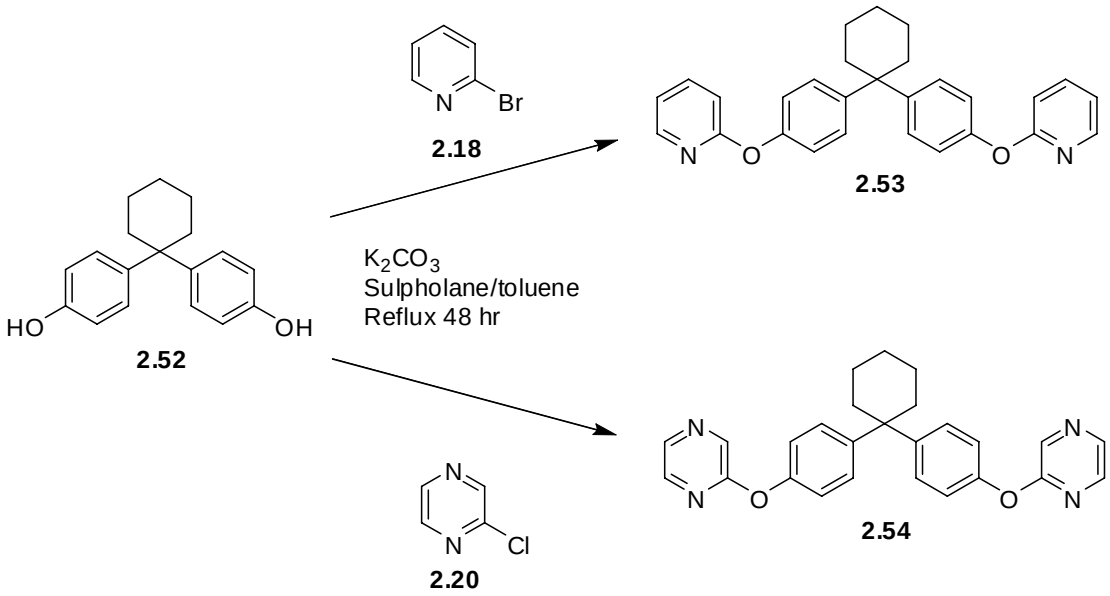
2.52

Figure 2.50 – *Structure of Bisphenol Z.*

Precursor **2.52** was synthesised by a simple acid-catalysed condensation of cyclohexanone with two equivalents of phenol. The method used to prepare the Bisphenol Z was adapted from a paper by Kolasa and co-workers, who used a similar procedure to prepare symmetrical compounds as inhibitors of leukotriene biosynthesis.[176] Cyclohexanone with an excess of phenol was mixed in a 1:1 solution of water and 1,4-dioxane. Concentrated sulfuric acid was slowly added to this solution. This method produced Bisphenol Z heavily contaminated with excess phenol. The ligand precursor **2.52** was then purified by column chromatography to remove the excess phenol, thus generating an off white solid in 38% yield. The ligand precursor **2.52** was initially synthesised by this method, while waiting for commercially available Bisphenol Z to arrive.

Symmetrical flexible ligands based around the Bisphenol Z backbone, with two independent benzene rings attached to separate nitrogen heterocycles are just as scarce as the Bisphenol A based ligands. Therefore, Bisphenol Z is another ideal ligand precursor for the construction and synthesis of a new range of symmetrical ligands. The adopted geometry and conformation of these Bisphenol Z based ligands and their complexes would be interesting to study.

The first two ligands synthesised with the Bisphenol Z backbone are shown in scheme 2.4. Ligands **2.53** and **2.54** were synthesised by the same nucleophilic substitution reactions as the previously discussed Bisphenol A derived ligands.[112] Ligands **2.53** and **2.54** were synthesised by double nucleophilic aromatic substitution of Bisphenol Z with the haloazines 2-bromopyridine (**2.18**) or 2-chloropyrazine (**2.20**) in a sulpholane/toluene (2:1) mixture under an inert atmosphere. Recrystallisation of crude ligands **2.53** and **2.54** from an acetone/water solution gave pure white solids in 70% and 82% yields, respectively. Subsequently, theses ligands were fully characterised by elemental analyses, mass spectrometry, melting points and ^{1}H NMR and ^{13}C NMR spectroscopy.[113]



Scheme 2.4 - *Synthesis of ligands **2.53** and **2.54** with the Bisphenol Z backbone.*

It is of interest to further investigate the conformations of these ligands in the solid state. Solid state structures will confirm their overall conformation and ligand structure. The distance between nitrogen donor atoms of a ligand is also another area of interest, because this can control the metal-metal separations in metal complexes. Therefore, attempts were made to grow single crystals suitable for X-ray crystallography with ligands **2.53** and **2.54**. Unfortunately X-ray quality crystals were only grown for ligand **2.54** and not **2.53**. Fortunately ligand **2.53** generated a number of metal complexes, which were investigated fully by X-ray crystallography.

Crystal structure of ligand 1,1-di(4-(2-pyrazinyloxy)phenyl)cyclohexane, 2.54

Pale yellow crystals of ligand **2.54** suitable for X-ray crystallography were obtained from the mother liquor from the recrystallisation. Ligand **2.54** crystallises in the monoclinic space group $P2_1/c$ with a full ligand molecule in the asymmetric unit. The asymmetric unit of ligand **2.54** is shown in figure 2.51, with the hydrogen atoms removed for clarity. In the solid state there is no observed symmetry. The two benzene rings and the cyclohexane ring twist around the central quaternary carbon of the Bisphenol Z backbone in a propeller type arrangement. The cyclohexane ring is in a locked conformation with one benzene ring in the equatorial position and one in the axial position. The pyrazine rings are facing almost perpendicular to the attached benzene rings, with the internal nitrogen atoms twisted inwards towards the centre of the cavity between the two benzene rings and the distal nitrogens point outwards. The overall shape of the ligand is seen in the low N-C-O-C torsional angles of 6.6° and 35.2°. The less hindered distal nitrogen atoms that are more likely to coordinate to metals have a distant separation of 13.350Å. The distance between the internal nitrogen atoms is only 8.020Å.

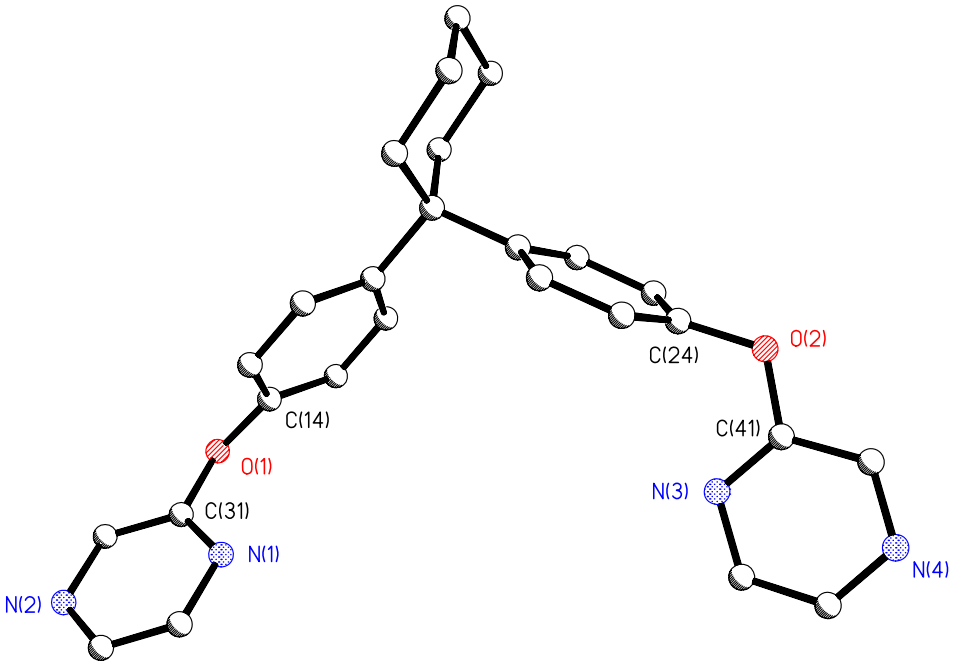
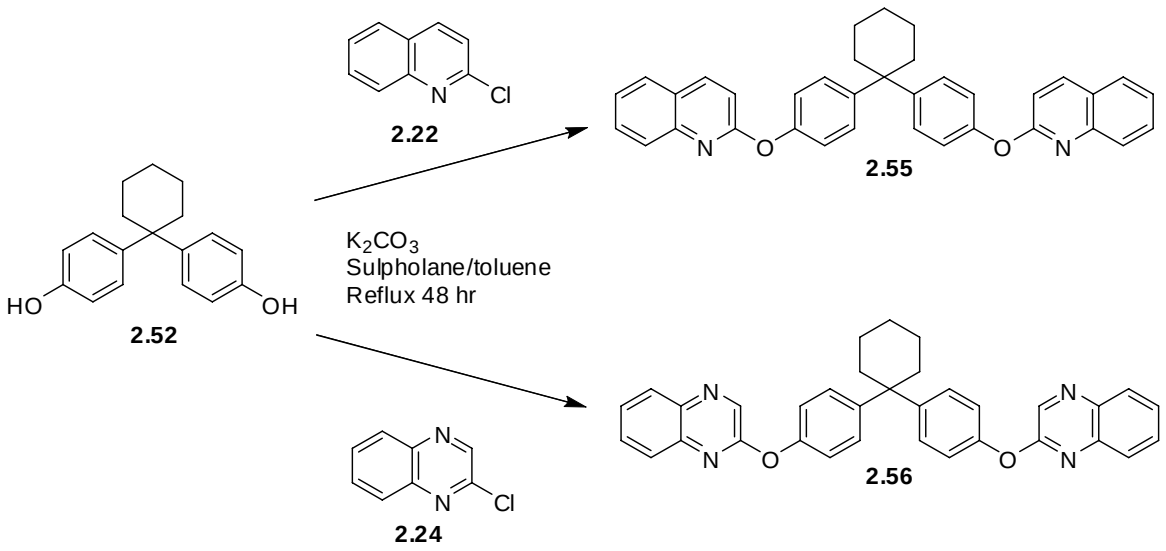


Figure 2.51 - *The crystal structure of ligand* **2.54** *with hydrogens omitted for clarity. Selected bond lengths (Å) and bond angles (°):C14-O1 1.412(2), O1-C31 1.378(2), N1-C31 1.315(3), C24-O2 1.412(2), O2-C41 1.373(2), N3-C41 1.315(2), C31-O1-C14 119.1(2), N1-C31-O1 119.7(2), C41-O2-C24 118.4(2), N3-C41-O2 120.2(2).*

In the molecular packing of **2.54**, the molecules pack with a few hydrogen bonding interactions. Due to the conformation of the ligand in the solid state there are no π-π stacking interactions. However, there are some edge-to-face interactions between benzene rings and pyrazine rings (2.549Å and 2.750Å).

Another two ligands were synthesised from the Bisphenol Z ligand precursor **2.52**, with 2-substituted quinoline or quinoxaline groups. These ligands have a larger heterocyclic system than the pyridine and pyrazine substituted ligands and it is therefore of interest to draw comparisons between them. Scheme 2.5 outlines the synthesis of new bridging ligands **2.55** and **2.56**. The diaryl ether linkages on ligands **2.55** and **2.56** were synthesised by double nucleophilic aromatic substitution of the Bisphenol Z ligand precursor **2.52** with 2-chloroquinoline (**2.22**) and 2-chloroquinoxaline (**2.24**) respectively.[112] This method is analogous to that used to prepare other similar ligands in this thesis. Recrystallisation of ligands **2.55** and **2.56** from acetone/water gave **2.55** as a yellow crystalline solid in 75% yield and **2.56** as a yellow solid in a smaller yield of 54%. Subsequently, these ligands were fully characterised by elemental analyses, mass spectrometry, melting points and ^{1}H NMR and ^{13}C NMR spectroscopy.[113]



Scheme 2.5 - *Synthesis of ligands **2.55** and **2.56** with the Bisphenol Z backbone.*

Crystals suitable for X-ray crystallography were grown for both ligands **2.55** and **2.56**, and the X-ray structures of these were determined to further investigate their conformations in the solid state.

Crystal structure of ligand 1,1-di(4-(2-quinolyloxy)phenyl)cyclohexane, 2.55

Pale yellow block-like crystals of ligand **2.55** were obtained by slow evaporation of an acetone/water solution. The crystals extinguished well and were found to be suitable for X-ray crystallography. X-ray analysis revealed the ligand to crystallise in the monoclinic space group $P2_1/c$ with a full molecule in the asymmetric unit and a severely disordered solvent molecule. The crystal structure of ligand **2.55** is shown in figure 2.52 with the hydrogens and disordered solvent molecule excluded for clarity.

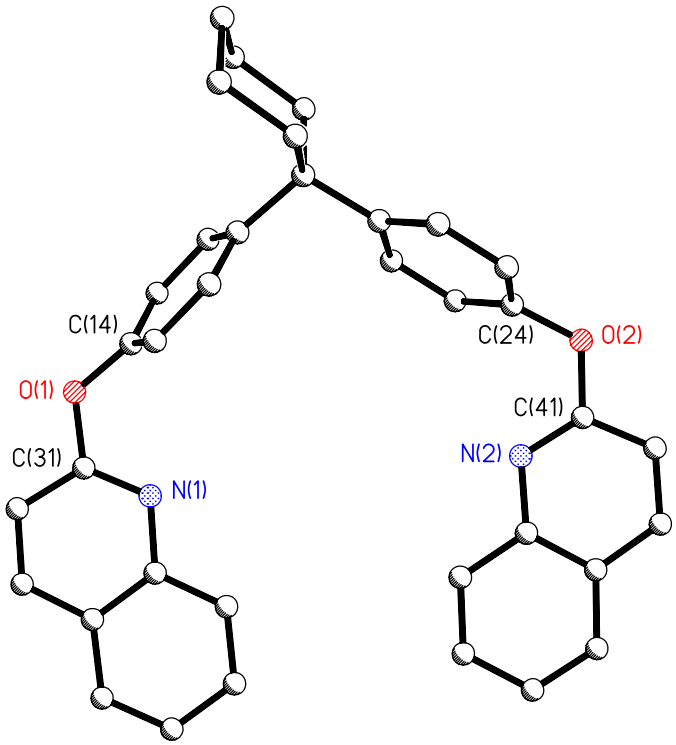


Figure 2.52 - *The crystal structure of ligand* ***2.55****. Selected bond lengths (Å) and bond angles (°): C14-O1 1.399(2), O1-C31 1.379(2), C31-N1 1.306(2), C24-O2 1.416(2), O2-C41 1.373(2), C41-N2 1.304(2), C31-O1-C14 120.1(1), N1-C31-O1 119.9(1), C41-O2-C24 117.9(1), N2-C41-O2 120.3(1).*

In the solid state the cyclohexane ring is locked in a chair conformation with the two benzene rings in the axial and equatorial positions about the central quaternary carbon. The quinoline rings are orthogonal to the attached benzene rings with the nitrogen donor atoms pointing inwards towards the centre of the cavity between the benzene rings, with only a small separation between the nitrogens of 6.657Å. The overall structure is non-planar with the two benzene rings in one plane and the two quinoline ring systems in the other; hence the quinoline rings are coplanar to each other. A space-filling diagram more clearly shows the conformation of ligand **2.55** in the solid state with its coplanar quinoline rings and small distance between nitrogen donor atoms, as depicted in figure 2.53. The way in which the quinoline rings are oriented to face each other with the two nitrogen atoms pointing inwards towards the center of the ligand makes it difficult for coordination of metals. In order for ligand **2.55** to bridge metals and construct metallosupramolecular species the quinoline rings would need to adopt quite a different conformation. However the solid state conformation suggests that this ligand might act as a chelating ligand to a single metal atom.

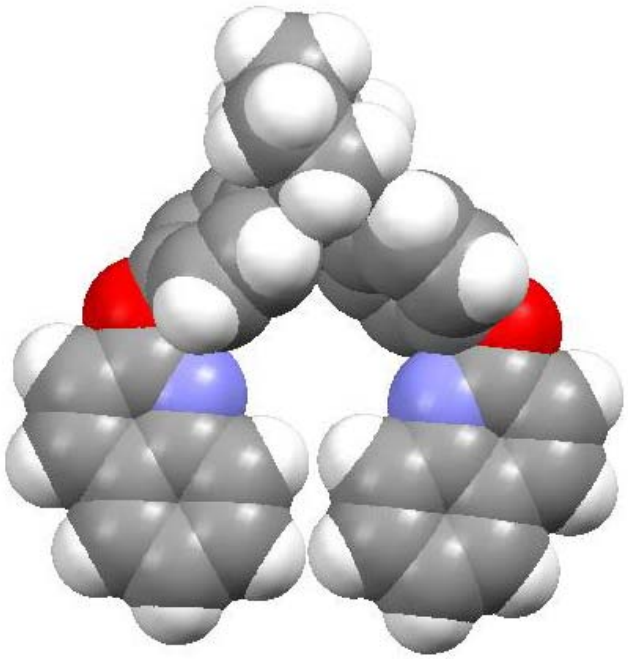


Figure 2.53 – *Space-filling diagram of ligand* ***2.55****.*

In the crystal packing there are extensive hydrogen bonding interactions between solvent and ligand molecules. There are also some edge-to-face interactions between

the benzene rings and quinoline rings of adjacent ligand molecules. These edge-to-face interactions range between 2.354Å and 2.764Å.

Crystal structure of ligand 1,1-di(4-(2-quinoxalinyloxy)phenyl)cyclohexane, 2.56

Yellow crystals suitable for X-ray crystallography were produced from a methanolic solution of ligand **2.56** and zinc chloride. Surprisingly, no complex formed and X-ray analysis revealed the presence of the free ligand **2.56**. Ligand **2.56** crystallises in the triclinic space group P-1 with a full molecule in the asymmetric unit. The structure of **2.56** is shown in figure 2.54, with the hydrogen atoms omitted for clarity. The structure of ligand **2.56** in the solid state has quite a different conformation to the previously mentioned 2-substituted quinoline ligand **2.55**, due to the orientations of the quinoxaline rings, which are perpendicular to the attached benzene rings. The two internal nitrogen donor atoms also point towards the center of the benzene rings, with a separation of 10.321Å. The less hindered nitrogens are pointing outwards facing in the opposite direction to the internal nitrogens with a greater separation of 14.694Å. These nitrogen atoms are more likely to coordinate to metals due to less steric hindrance. The twisted conformation seen in the ligand is reflected in the low N-C-O-C torsional angles of 11.1° and 13.7°.

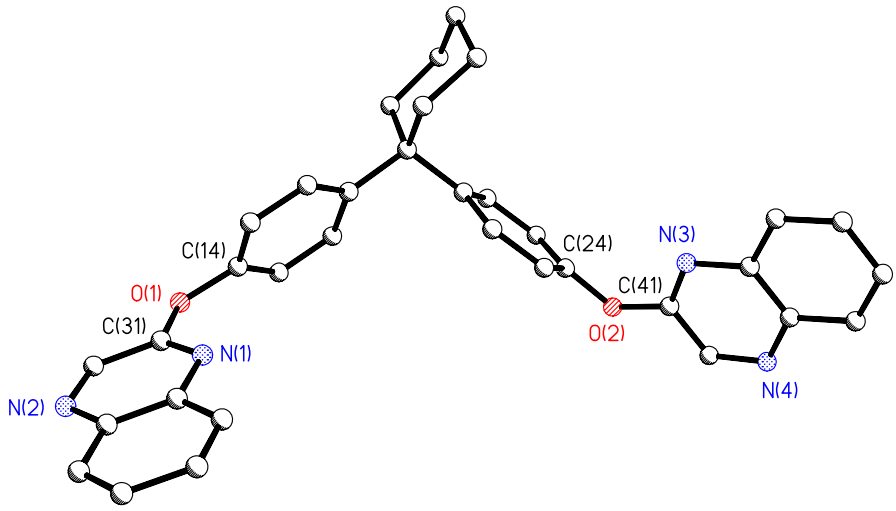


Figure 2.54 - *The crystal structure of ligand* ***2.56.*** *Selected bond lengths (Å) and bond angles (°): C14-O1 1.406(2), O1-C31 1.361(2), C31-N1 1.293(2), C24-O2 1.404(2), O2-C41 1.360(2), C41-N3 1.293(2), C31-O1-C14 118.9(1), N1-C31-O1 121.2(1), C41-O2-C24 120.1(1), N3-C41-O2 122.0(1).*

In the crystal packing, there are numerous hydrogen bonding interactions between ligand molecules. There are also some edge-to-face interactions between adjacent quinoxaline rings (2.766Å) and facially arranged benzene rings also interact via edge-to-face interactions with adjacent quinoxaline rings (2.746Å).

A literature review revealed only a few compounds that are closely related to the Bisphenol Z based ligands **2.53**, **2.54**, **2.55** and **2.56**. Figure 2.55 shows some examples of ligands from the literature that are structurally similar to the Bisphenol Z ligands described above that have been used as synthons to construct metallosupramolecular arrays. Ligand **2.57** is very similar to the Bisphenol Z ligands mentioned above having the same Bisphenol Z backbone with alkyne groups attached, as opposed to nitrogen containing heterocycles. McArdle et al. have also made complexes with ligands similar to **2.57** with different hinge groups to cyclohexane. Some of these complexes were made from ligands containing the Bisphenol A-type backbone and have already been discussed (ligands **2.26** and **2.27**). Ligand **2.57** was converted to a dialkynyldigold(I) precursor, which was then reacted with a diphosphine ligand to yield a unique double-braided [2]catenane.[115, 177] This is believed to be the first X-ray structure of a doubly-braided catenane. Variable temperature NMR experiments were carried out on the catenane that showed a molecular switching motion of the complex. In 2003, van der Vlugt et al. described the synthesis of a new range of diphosphine ligands based around the previously neglected Bisphenol Z backbone core, such as ligand **2.58** in figure 2.55.[178, 179] They also described the synthesis of various other diphosphine ligands based around other Bisphenol-type backbones.[178, 179] Van der Vlugt et al. reacted ligand **2.58** with palladium, platinum and rhodium precursors to yield a series of dimeric macrocycles that were characterised by X-ray crystallography.[179] Each of the dimeric macrocycles coordinated to the metal atom through the phosphorus atoms and displayed *trans*-coordination.

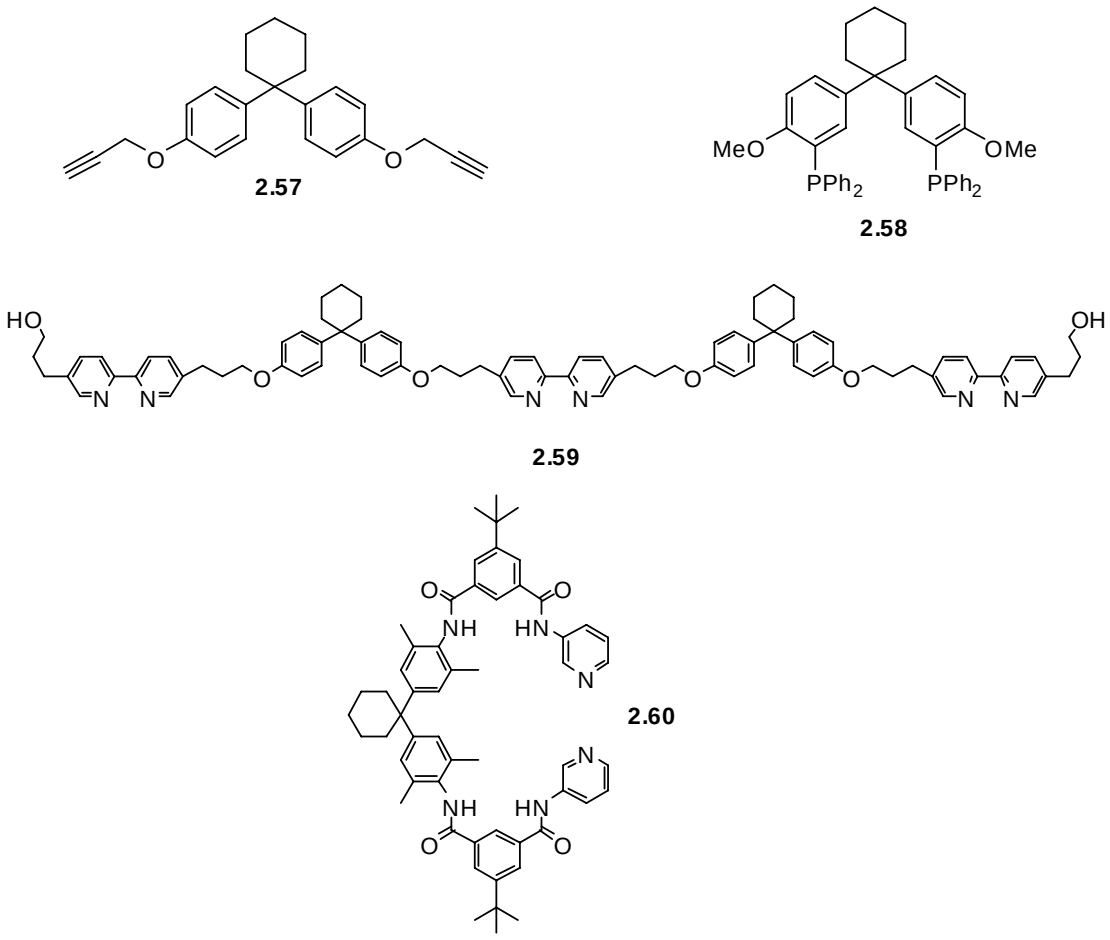


Figure 2.55 - *Examples of previously reported Bisphenol Z based ligands.*

Ligand **2.59** is an example of a ligand displaying some structural similarities to the Bisphenol Z based ligands with Bisphenol Z groups covalently joined by rigid bipyridine linker subunits. Hunter and Mayers reported the reaction of ligand **2.59** with $Zn(ClO_4)_2$ to give an open knot architecture with the zinc ion coordination organising the central core of the knot.[180] What is even more interesting is that this process is reversible. If one reacts ligand **2.59** with $Zn(ClO_4)_2$ the knot forms and if one then adds chloride the knot is unfolded. Subsequent addition of silver ions refolds the knot architecture. Ligand **2.60** is another example of a ligand that is structurally similar with a central Bisphenol Z core with amide nitrogens instead of oxygen atoms. Complexation of ligand **2.60** with palladium yielded an interlocked [2]catenane metallosupramolecular species.[181] Further experiments revealed that the catenation of the two macrocyclic rings is a reversible process that can be controlled by using different solvents. Therefore, further research is currently being carried out into investigating the potential use of this complex as a molecule switch and shuttle.

Ligands **2.53**, **2.54**, **2.55**, and **2.56** were used as synthons and reacted with metal salts in the hope of constructing fascinating metal coordination compounds.

Complexes with ligand 2.53

*Crystal structure of the complex with $CoCl_2$ (**2.61**)*

Within minutes of mixing an acetone solution of ligand **2.53** and cobalt(II) chloride clusters of blue crystals formed. Unfortunately, most of the crystals were not suitable for X-ray crystallography, because they were very thin needle-like crystals that shattered on contact. However, there were a number of thicker plates that were suitable for X-ray crystallography. Unfortunately, the crystal that was mounted for X-ray structure determination was not the best quality and although the diffraction patterns were reasonable the crystal showed signs of decomposing as well as possible twinning. This is not surprising considering that the crystals grew within minutes of mixing. Crystals that grow this fast tend to cluster on top of each other and consequently it is hard for true single crystals to form. On the other hand, crystals that take more than a couple of days to form are more likely to exist as single crystals. Despite this enough data was collected to solve the structure and give a reasonable refinement with an R_1 value of 10.74%.

The structure solved in the triclinic space group P-1, with one ligand molecule, one metal atom, two disordered chlorine atoms and partially disordered acetone and ethanol solvent molecules in the asymmetric unit. X-ray analysis revealed a one-dimensional helical coordination polymer, a section of which is shown in figure 2.56. This shows the connectivity of the atoms in the helical coordination polymer with the hydrogens and disordered solvent molecules removed for clarity. The chlorine atoms are disordered over two sites with the major contributing chlorine atoms occupied 90% of the time.

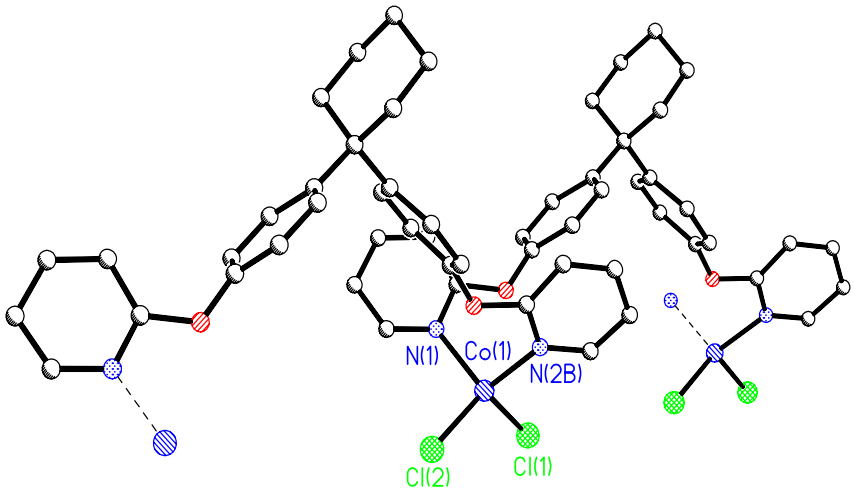


Figure 2.56 – *A section of the one-dimensional helical coordination polymer* ***2.61****. The minor 10% component of the disordered chlorine atoms is not shown. Selected bond lengths (Å) and bond angles (°):Co1-N1 2.065(7), Co1-N2B 2.054(8), Co1-Cl1 2.242(3), Co1-Cl2 2.247(3), N2B-Co1-N1 104.3(3), N1-Co1-Cl1 115.5(2), N1-Co1-Cl2 104.1(2), N2B-Co1-Cl1 104.2(2), N2B-Co1-Cl2 115.9(2), Cl2-Co1-Cl1 112.9(1).*

The one-dimensional helical coordination polymer is very similar to the several coordination polymers that formed with the 2-pyridine substituted Bisphenol A backboned ligand **2.19** previously discussed. The only difference between ligands **2.19** and **2.53** is the different 'hinge' groups on the Bisphenol backbone. Ligand **2.19** is derived from Bisphenol A and therefore has a central propane group whereas ligand **2.53** has a cyclohexane group as the central hinge group.

The cobalt atom coordinates to two pyridine nitrogens from two separate ligands and to two chlorine atoms. The geometry of the cobalt atom is distorted tetrahedral, which is accentuated by the disorder of the two chlorine atoms. The major component has the largest deviation from tetrahedral of 115.9° (N1-Co1-Cl2). The Co-N bond lengths are 2.054Å and 2.065Å and the Co-Cl bond lengths of the major component are 2.242Å and 2.247Å. The Co-Cl bond lengths of the minor component were found to be a little longer than that of the major component, with distances of 2.274Å and 2.306Å.

In the crystal structure the cyclohexane ring is locked in a chair conformation with the two benzene rings in the axial and equatorial positions about the central quaternary carbon. The ligand has a concave shape and has a similar 'V-type' arrangement to that

of other Bisphenol Z derived ligands, with the two aromatic benzene groups acting as the arms of the 'V' linked via the central quaternary carbon atom. The pyridine rings of the ligand are almost perpendicular to the attached benzene rings and lie on the same side of the 'V' shaped Bisphenol Z backbone, with the nitrogen atoms twisted to point outwards in order to allow the pyridine rings to wrap around the cobalt atoms in a helical manner.

The one-dimensional helical polymer propagates down the helical b-axis, with each section of the polymer a translation from the previous. Since the ligand is achiral and the complex crystallises in a centrosymmetric space group, the structure contains both P(right-handed) and M(left-handed) helices that are related by symmetry. An illustration of one of the helices is shown in figure 2.57, with the hydrogens and solvent molecules removed for clarity. The helices have a pitch of 12.140Å, which is equal to the length of the b-edge of the unit cell and corresponds to the distance between two cobalt atoms in a helical chain. The topology seen in this cobalt helix is very similar to that seen in the helical coordination polymers formed with Bisphenol A derived ligand **2.19**.

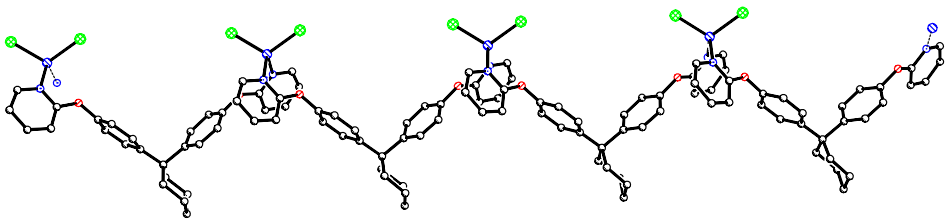


Figure 2.57 – *A perspective view of the one-dimensional helical coordination polymer* ***2.61***.

The one-dimensional helical strands pack with only a few edge-to-face interactions between the two enantiomeric helical strands. There are several hydrogen bonding interactions between various hydrogens of the ligand molecule and chlorine atoms of adjacent polymer strands. The solvent molecules interact with polymer strands through hydrogen bonds and other short contacts.

*Crystal structure of the complex with $CuCl_2$ (**2.62**)*

Slow evaporation of a solution containing ligand **2.53** and copper(II) chloride produced beautiful blue rod-like crystals after a week of standing. These blue crystals extinguished well under the microscope and were perfect crystals for X-ray crystallography and the structure solved accordingly. The complex crystallises in the monoclinic space group $P2_1/n$ with two ligand molecules, two $CuCl_2$ units and one methanol solvent molecule in the asymmetric unit. The asymmetric unit is shown in figure 2.58 with the hydrogens and solvent molecule removed for clarity. X-ray analysis revealed a unique and fascinating one-dimensional necklace polymer. The pyridine binding arms of each of the ligands are facing in opposite directions and are once again perpendicular to the attached benzene rings. The two nitrogen atoms of each of the pyridine binding arms are pointing away from the central cavity between the two benzene rings in order to be able to twist and coordinate to the copper atoms.

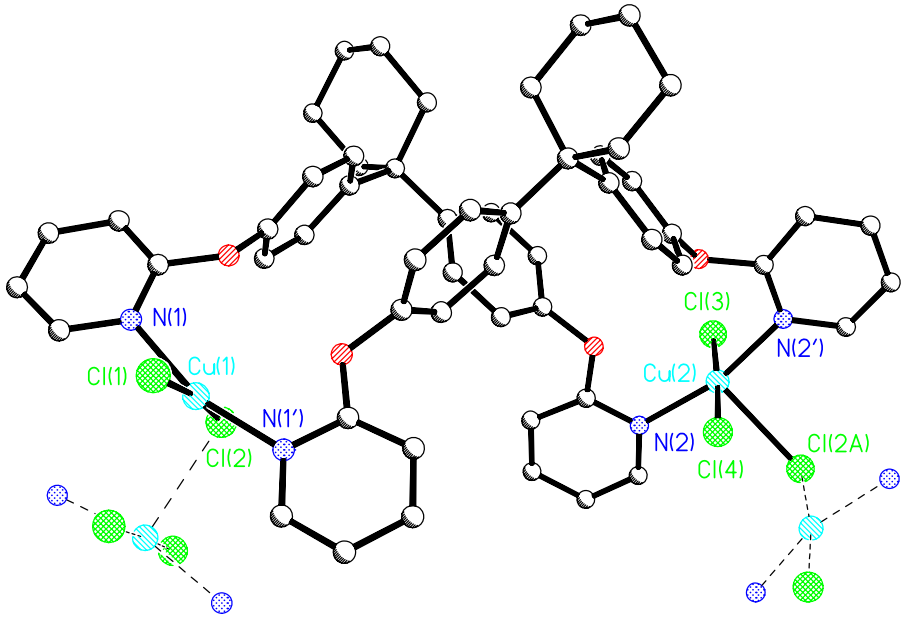


Figure 2.58 – *Contents of the asymmetric unit of complex **2.62**. Selected bond lengths (Å) and bond angles (°): Cu1-N1 2.011(2), Cu1-N1' 2.018(2), Cu1-Cl1 2.2627(6), Cu1-Cl2 2.3234(6), Cu2-N2' 2.021(2), Cu2-N2 2.022(2), Cu2-Cl3 2.2772(5), Cu2-Cl4 2.3264(5), Cu2-Cl2A 2.7202(5), N1-Cu1-N1' 163.00(7), N1-Cu1-Cl1 89.91(5), N1'-Cu1-Cl1 90.60(5), N1-Cu1-Cl2 88.01(5), N1'-Cu1-Cl2 93.54(5), Cl1-Cu1-Cl2 172.37(2), N2'-Cu2-N2 165.79(7), N2'-Cu2-Cl3 88.84(5), N2-Cu2-Cl3 88.55(5), N2'-Cu2-Cl4 91.99(5), N2-Cu2-Cl4 90.01(5), Cl3-Cu2-Cl4 177.26(2), N2'-Cu2-Cl2A 94.76(5), N2-Cu2-Cl2A 99.42(5), Cl3-Cu2-Cl2A 96.98(2), Cl4-Cu2-Cl2A 85.55(2).*

In complex **2.61** there are two independent copper atoms, each with different coordination geometries. Each of the copper(II) atoms is coordinated to two nitrogen atoms from separate ligand stands. One of the copper atoms (Cu1) is four-coordinate binding two pyridine nitrogen atoms and two chlorine atoms. The other copper atom (Cu2) is five–coordinate and binds to two pyridine nitrogens from separate ligands and three chlorine atoms. One of the chlorine atoms (Cl2) acts as a bridge between the two copper atoms. Figure 2.59 shows the two copper(II) atoms bridged by a chlorine atom complex **2.61**. The bridging of a chlorine atom between two copper(II) atoms with different coordination geometries is unusual and a literature review revealed only one other binuclear copper chloride complex with a similar coordination motif.[182] Zhang et al. designed a binuclear copper(II) chloride complex with the ligand 1,10-phenanthroline that exhibited two different copper(II) atoms with different coordination geometries bridged by a chlorine atom. This complex was used to study the interaction of such copper complexes with DNA.[182]

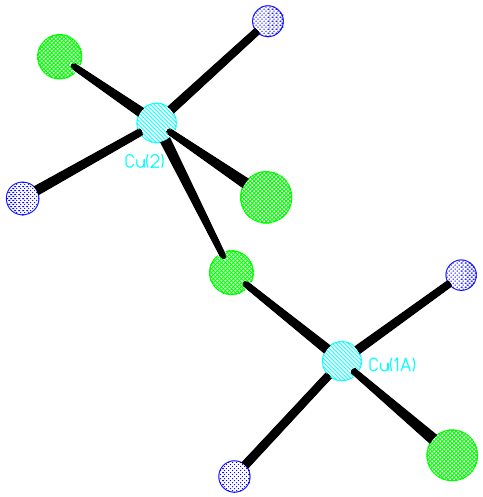


Figure 2.59 – *Perspective view of the two copper(II) atoms each with two different coordination geometries bridged by a single chlorine atom.*

The Cu1 atom has a distorted square planar coordination geometry which is formed by two nitrogen atoms from separate ligands and one monodentate chlorine atom (Cl1) and a bridging chlorine atom (Cl2). The two nitrogens from the pyridine ligands and the two chlorine atoms form a distorted CuN_2Cl_2 plane. The Cu-N bond lengths about Cu1 are 2.011Å and 2.018Å, which are within the same range of the copper complex reported by Zhang et al.[182] The Cu-Cl bond lengths are 2.263Å and 2.323Å, which are longer

than the Cu-N bond lengths, but still similar to the previously reported dinuclear copper complex. The Cu2 atom has a distorted square-pyramidal environment binding to two pyridine nitrogens, two monodentate chlorine atoms (Cl3 and Cl4) and the bridging chlorine atom (Cl2). Two nitrogen atoms from separate pyridine ligands and two of the chlorine atoms form the N_2Cl_2 basal plane. The apical position is occupied by a bridging chlorine atom. The Cu-N bond lengths about Cu2 are 2.022Å and 2.021Å and the Cu-Cl bond lengths are 2.277Å and 2.326Å. Once again the Cu-Cl bond lengths are longer than the Cu-N bond lengths and similar to the complex reported by Zhang et al.[182] The bridging chlorine atom in the apical position has a significantly longer bond length of 2.720Å (Cu2-Cl2A), which indicates the presence of Jahn-Teller distortion. The distance between the bridging chlorine atom and the four-coordinate copper atom is much shorter than that between the square-pyramidal copper atom and the bridging chlorine atom. In fact the bond length between the square-pyramidal copper atom and the bridging chlorine atom is the longest Cu-Cl bond in the complex and is therefore also the weakest. The distance between copper atoms in the copper motif is 3.853Å.

The resulting complex is a 'necklace' type polymer, which is a one-dimensional polymeric chain composed of M_2L_2 macrocyclic units linked by the unique copper motif described above. Each macrocyclic unit is composed of two ligands bound to two copper atoms resulting in a 32-membered M_2L_2 macrocycle. The distance between copper atoms across the macrocycle is 12.491Å (Cu1-Cu2). Each macrocyclic unit also has a concave curvature to it, which is accentuated by the 'V' shaped conformation of the ligands. There is no cavity or space in the macrocycle, due to the conformation and orientation of the two ligands of the macrocycle. The polymer propagates in an undulating fashion in one-dimension. Each macrocyclic unit acts as a concave bridge with the copper atoms connected to two such macrocyclic units by a two-fold screw axis. The M_2L_2 macrocyclic units flip orientation between the bridging copper chloride motifs, so that each bridging copper chloride motif is coordinated to a macrocyclic unit above and a macrocyclic unit below it. As a result, the macrocyclic units alternate in orientation along the chain to give an undulating necklace polymer. A section of the polymer is shown in figure 2.60 with the hydrogens and solvent molecules omitted for clarity.

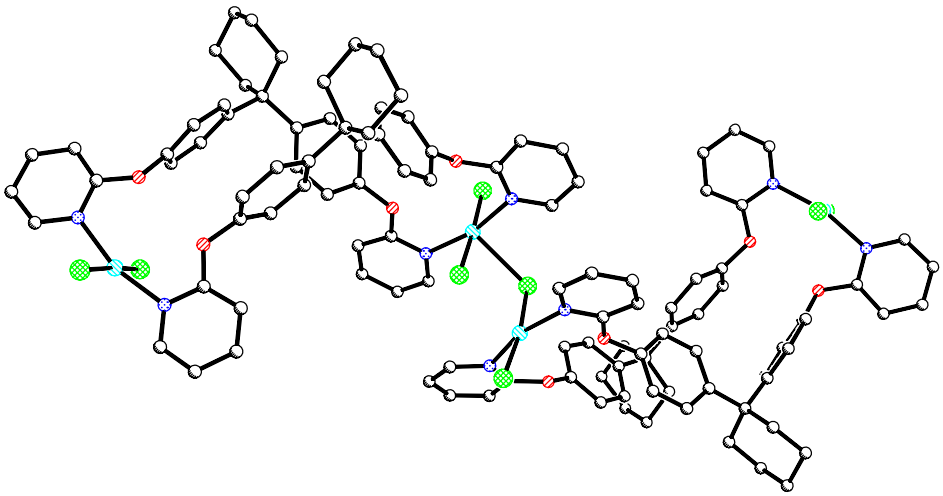
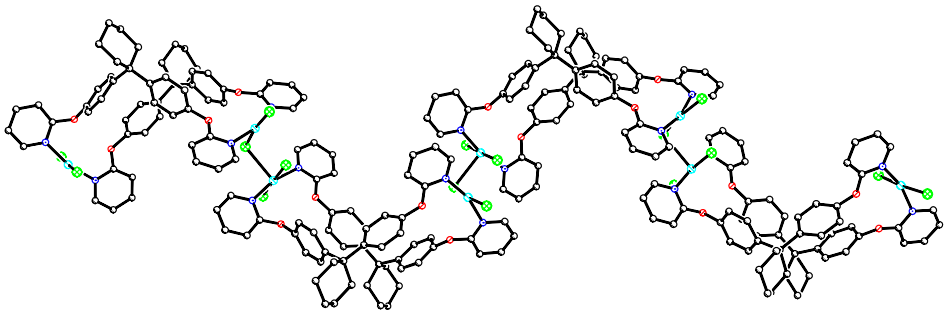
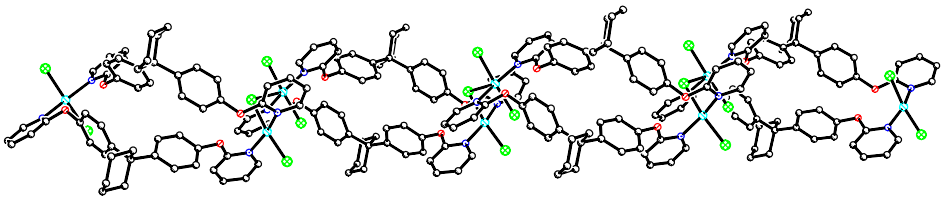


Figure 2.60 – *A section of the one-dimensional coordination polymer* ***2.62***.

The M_2L_2 macrocyclic units propagate in an alternating coil-like manner with one macrocycle oriented to face upwards and one macrocycle facing downwards along the chain. Each of the M_2L_2 macrocycles is inter-linked by the bridging copper chloride motif that lies perpendicular to the joining macrocycles. A side-on view of the necklace polymer illustrating this is shown in figure 2.61(a). Figure 2.61(b) shows a bird's eye view of the complex, when looking from above. The bird's eye view depicts the macrocyclic units linked by copper atoms bridging a chlorine atom. Consequently, the topology of complex **2.62** is not a continuous chain with big rings (the M_2L_2 macrocycles) that are inter-linked by smaller rings, like complex **2.37**. Instead complex **2.62** has M_2L_2 macrocycles that are connected through their copper atoms via a single strand.



(a)



(b)

Figure 2.61 – ***(a)*** *Side on view of complex* ***2.62****.* ***(b)*** *Bird's eye view of complex* ***2.62*** *when viewed from above. The hydrogens and solvent molecules have been removed for clarity.*

Complex **2.62** is very similar to that of complex **2.37** made from the Bisphenol A based ligand. These complexes are almost identical, being prepared under the same conditions with the same two solvents, methanol and dichloromethane, used to aid crystallisation. Both complexes form a 'necklace' type polymer with copper chloride composed of M_2L_2 macrocyclic units linked by the unique copper motifs. In both complexes, each macrocyclic unit is composed of two ligands bound to two copper atoms to generate a 32-membered M_2L_2 macrocycle. Each M_2L_2 macrocyclic unit in both complexes also has a concave curvature to it and propagates in an undulating fashion in one-dimension. The main difference between the two complexes is the bridging copper chloride motif. The copper atoms in complex **2.37** have square-pyramidal environments that give rise to Cu_2Cl_4 squares which link together M_2L_2 macrocyclic units. In comparison the two copper(II) atoms in complex **2.62** have different coordination geometries, both 4-coordinate and 5-coordinate, that are bridged by a single chlorine atom, which link together the M_2L_2 macrocyclic units.

In the crystal packing there are a few interactions between the methanol solvent molecule and ligand chains. There is no π-π stacking between benzene rings within a macrocyclic unit, because of the ligand conformation and orientation in the solid state. The chains stack with numerous hydrogen bonding interactions involving hydrogens from the ligand molecules. The chlorines also interact with hydrogen atoms of ligands from adjacent necklace strands.

*Crystal structure of the complex with $ZnBr_2$ (**2.63**)*

Zinc bromide was dissolved in methanol and layered upon a solution of ligand **2.53** in dichloromethane. Slow evaporation of this solution furnished colourless plate-like crystals that were suitable for X-ray crystallography. The complex crystallises in the centrosymmetric space group P-1. The asymmetric unit contains one ligand molecule, one $ZnBr_2$ and a disordered dichloromethane solvent molecule. An expanded view of the asymmetric unit to show the zinc atom connectivity is shown in figure 2.62, with the hydrogens and solvent molecules removed for clarity. Although the crystals that were put up for X-ray crystallography extinguished well under the microscope they gave weak diffraction patterns. The difference map also showed large peaks around the zinc atom suggesting the presence of other low occupancy coordinated atoms to zinc. Consequently, the structure only refined to an R_1 value of 7.89%. The X-ray analysis revealed another one-dimensional helical coordination polymer with ligand **2.53**, but with a different metal.

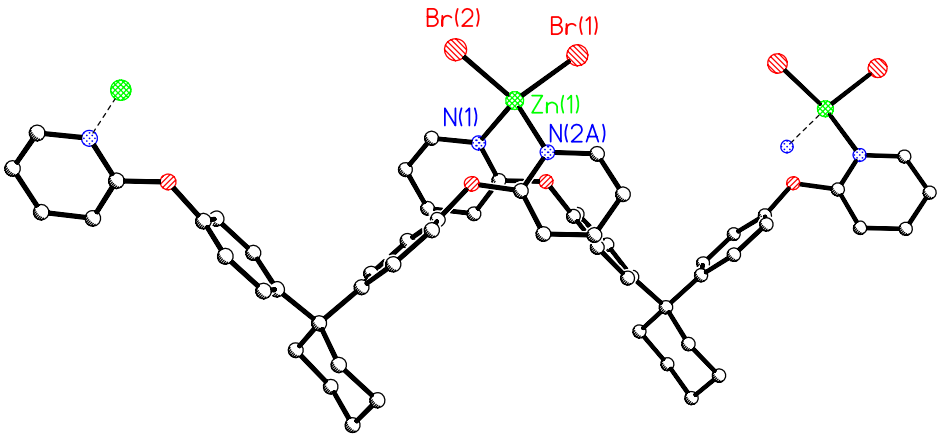


Figure 2.62 – *A section of the one-dimensional helical coordination polymer **2.63**. Selected bond lengths (Å) and bond angles (°): Zn1-N1 2.075(7), Zn1-N2A 2.072(7), Zn1-Br1 2.382(2), Zn1-Br2 2.381(2), N2A-Zn1-N1 101.6(3), N1-Zn1-Br1 114.6(2), N1-Zn1-Br2 106.8(2), N2A-Zn1-Br1 106.5(2), N2A-Zn1-Br2 115.6(2), Br2-Zn1-Br1 111.55(6).*

Crystals that are isomorphous have almost identical crystal structures, with some atoms replaced by chemically similar ones, such as chlorine atoms replace by bromine atoms. The zinc one-dimensional helical coordination polymer **2.63** is isomorphous but not quite isostructural to the previously mentioned one-dimensional helical coordination polymer made with $CoCl_2$ (**2.61**). Also, the topology seen in this zinc helicate is very

similar to that seen in the one-dimensional helical coordination polymers formed with Bisphenol A derived ligand **2.19**. In the crystal structure the cyclohexane ring is in a locked chair conformation with the two benzene rings in the axial and equatorial positions about the central quaternary carbon. The ligand has a concave shape and has a similar 'V-type' arrangement with the two aromatic benzene groups acting as the arms of the 'V' linked via the central quaternary carbon atom. The pyridine rings are almost perpendicular to the attached benzene rings of the ligand and lie on the same side of the 'V' shaped Bisphenol Z backbone, with the nitrogen atoms twisted to point outwards in order to allow the pyridine rings to wrap around the zinc atoms in a helical fashion.

In complex **2.63** the zinc atom is 4-coordinate, being coordinated by pyridine nitrogen atoms of two separate ligands and two bromine counterions. The coordination geometry of zinc is distorted tetrahedral with the largest deviation from tetrahedral being 115.6° (Br2-Zn1-N2A). The tetrahedral geometry is possibly distorted due to the presence of other unidentified low occupancy coordinated atoms around the zinc. The Zn-N bond lengths are 2.072Å and 2.075Å and the Zn-Br bond lengths are 2.381Å and 2.382Å, which are similar to the bond lengths of other zinc bromide complexes reported in this thesis.

Overall, the helical zinc polymer **2.63** has a very similar structure to that of the cobalt helical coordination polymer **2.61**. In complex **2.63**, one-dimensional helical strands propagate down the b-axis, with each polymer section a translation from the previous. An illustration of a larger section of one of the helices is shown in figure 2.63, with the hydrogens and solvent molecules removed for clarity. The structure contains both P(right-handed) and M(left-handed) helices in the space group P-1. The helices have a pitch of 12.280Å, which is equal to the length of the b-edge of the unit cell. The pitch in the zinc complex **2.63** corresponds to the distance between two zinc atoms in a helical chain and the distance taken by one ligand and one zinc atom to complete a full 360° turn about the helical axis.

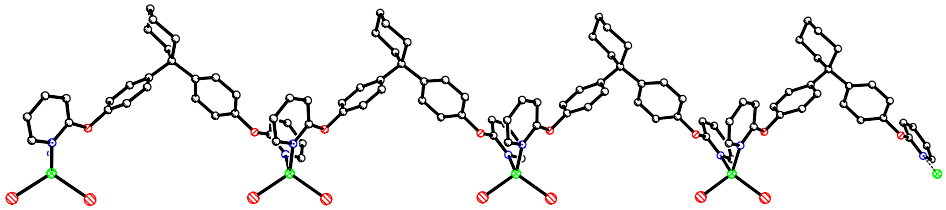


Figure 2.63 – *A perspective view of the one-dimensional helical coordination polymer* ***2.63****.*

*Crystal structure of the complex with $ZnCl_2$ (**2.64**)*

Attempts were made to prepare a similar helical coordination polymer to complex **2.63** with no disorder in the crystal structure. Therefore, ligand **2.53** was reacted with zinc chloride under the same conditions as complex **2.63** to yield colourless plate-like crystals that were suitable for X-ray crystallography. Unfortunately the crystals were very thin brittle plates that broke easily and therefore it took some patience and time to mount a single crystal. Luckily X-ray analysis revealed another one-dimensional helical coordination polymer similar to the zinc bromide helical polymer **2.63** discussed above. The crystal structures are almost identical to each other. In fact, complex **2.64** is isomorphous to complex **2.63**. The similarities do not end there; in complex **2.64** the difference map also shows large peaks around the zinc atom suggesting the presence of other low occupancy coordinated atoms to zinc. Consequently, this structure only refined down to an R_1 value of 8.97%. These large peaks around the zinc atom were also seen in complex **2.63**. Therefore, although an almost identical helical coordination polymer was made from $ZnCl_2$ it was still found to have the same problems as the $ZnBr_2$ helical complex (**2.63**). The asymmetric unit contains one ligand molecule, one $ZnCl_2$ and a water molecule. An extended view of the asymmetric unit to show the zinc atoms connectivity is shown in figure 2.64, with the hydrogens and water molecules omitted for clarity. Complex **2.64** is very similar to the previously discussed complex **2.63**; therefore a different view of the helical coordination polymer is shown in figure 2.64.

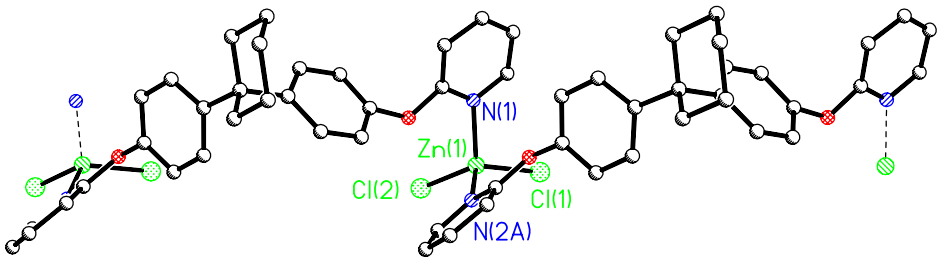


Figure 2.64 - *A section of the one-dimensional helical coordination polymer* ***2.64****. Selected bond lengths (Å) and bond angles (°): Zn1-N1 2.065(8), Zn1-N2A 2.060(8), Zn1-Cl1 2.229(3), Zn1-Cl2 2.225(3), N2A-Zn1-N1 101.4(3), N1-Zn1-Cl1 105.7(2), N1-Zn1-Cl2 116.1(2), N2A-Zn1-Cl1 114.9(2), N2A-Zn1-Cl2 105.8(2), Cl2-Zn1-Cl1 112.6(1).*

The zinc atom coordinates to two pyridine nitrogens and two chlorine atoms with a distorted tetrahedral geometry. The largest deviation from the tetrahedral geometry is 116.1° (N1-Zn1-Cl2). The Zn-N bond lengths are 2.060Å and 2.065Å and the Zn-Cl bond lengths are 2.225Å and 2.229Å, which are similar to the bond lengths of other helical zinc complexes reported so far in this thesis. In complex **2.64** the cyclohexane ring is locked in a chair conformation with the two benzene rings in the axial and equatorial positions about the central quaternary carbon. Both pyridine bonding arms of the ligand lie on the same side of the 'V' shaped Bisphenol Z backbone and are positioned to point outwards. The pyridine groups are once again perpendicular to the attached benzene rings allowing the pyridine rings to wrap around the zinc atoms in a helical fashion.

The helix propagates down the b-axis in one-dimension in helical chains. Each of the repetitive units of the helical chain is related by translation from the previous. An illustration of a larger section of one of the helices from a different view point to previous helices is shown in figure 2.65, with the hydrogens and solvent molecules omitted for clarity. Since the ligand is achiral and the complex crystallises in a centrosymmetric space group, the structure must contain both P(right-handed) and M(left-handed) helices that are related by symmetry. The helices have a pitch of 12.209Å, which is equal to the length of the b-edge of the unit cell. Once again the pitch corresponds to the distance traversed between two zinc atoms in a helical chain.

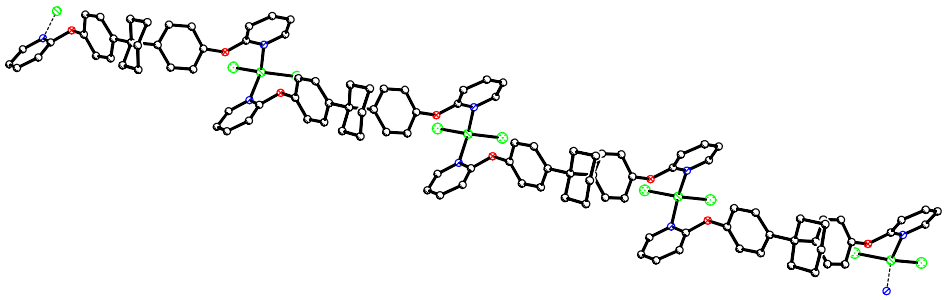


Figure 2.65 – *Perspective view of a larger section of the one-dimensional helical coordination polymer* ***2.64****.*

Other complexes with ligand ***2.53***

Ligand **2.53** was reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgCF_3SO_3$, $AgBF_4$, $AgClO_4$, $PdCl_2$, $PdCl_2(PhCN)_2$, $ZnBr_2$ and $ZnCl_2$ under a variety of different conditions. Complexation of ligand **2.53** with some of these metal salts gave X-ray quality crystals, which have already been discussed in some detail. Unfortunately, X-ray quality crystals or crystalline solids were not formed with all of these metals. Some of the complexes gave precipitates immediately, however despite several attempts most of these complexes could not be recrystallised and were not analysed any further.

Reaction of ligand **2.53** with CuI gave a bronze coloured crystalline solid. Elemental analysis revealed a complex with a 2:1 ratio of metal to ligand. This 2:1 ratio suggests the possible formation of a discrete complex or even more likely a one-dimensional polymer composed of ligands linked to Cu_2I_2 squares. The formation of Cu_2I_2 squares is quite common in CuI crystal structures.[27]

Reaction of ligand **2.53** with $Cu(ClO_4)_2$ and $AgPF_6$ gave complexes having a 1:1 ratio which could correspond to the formation of a discrete or a polymeric structure. This polymeric structure could be just a one-dimensional polymer or perhaps a helical one-dimensional polymer similar to that formed with $CoCl_2$ and the zinc salts.

A fine colourless crystalline solid formed on reaction of ligand **2.53** with $AgClO_4$. Elemental analysis revealed a complex with a 2:1 ratio of metal to ligand.

Complexes with ligand 2.54

*Crystal structure of the complex with CuI (**2.65**)*

A solution of copper iodide was dissolved in acetonitrile and carefully layered on top of a solution of ligand **2.54** dissolved in dichloromethane. Slow evaporation of the resulting yellow solution produced beautiful yellow block-like crystals suitable for X-ray crystallography. The crystals were clustered together into large clumps that had to be broken apart and separated out in order to find a single crystal. The complex crystallises in the monoclinic space group C2/c with one ligand molecule and one CuI in the asymmetric unit, as depicted in figure 2.66, with the hydrogens omitted for clarity.

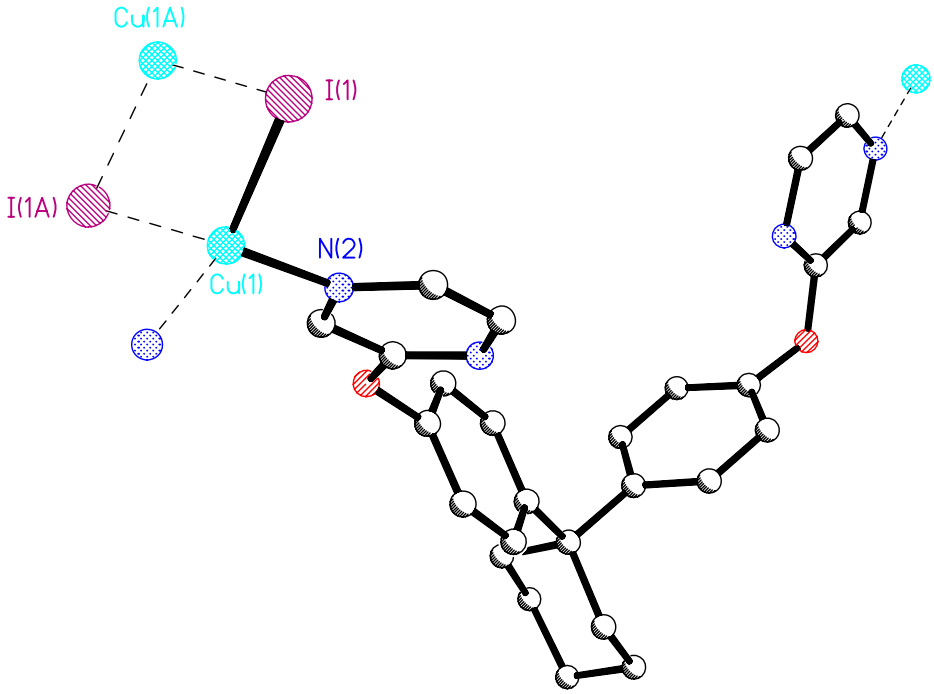


Figure 2.66 – *Contents of the asymmetric unit of complex **2.65**. Selected bond lengths (Å) and bond angles (°): Cu1-N2 2.021(1), Cu1-N4B 2.048(1), I1-Cu1 2.626(3), I1A-Cu1 2.675(3), Cu1-I1-Cu1A 60.530(8), Cu1A-Cu1-I1A 58.835(8), N2-Cu1-N4B 122.69(5), N2-Cu1-I1 108.54(4), N4B-Cu1-I1 103.67(4), N2-Cu1-Cu1A 117.51(4), N4B-Cu1-Cu1A 119.48(4), I1-Cu1-Cu1A 60.635(9), N2-Cu1-I1A 103.76(4), N4B-Cu1-I1A 99.94(4), I1-Cu1-I1A 119.134(8).*

In complex **2.65** the two benzene rings and the cyclohexane ring twist around the central quaternary carbon of the Bisphenol Z backbone in a propeller type arrangement.

The cyclohexane ring is in a locked chair conformation with one benzene ring in the equatorial position and one in the axial position. The pyrazine rings of the ligand are facing almost perpendicular to the attached benzene rings, with the internal nitrogen atoms twisted to point inwards towards the centre of the cavity between the two benzene rings and the distal nitrogens point outwards in order to bind to the copper metal atoms. Both pyrazine binding arms of the ligand lie on the same side of the 'V' shaped Bisphenol Z backbone. The conformation of the ligand in complex **2.65** is the same as that of the free ligand in the solid state.

The copper atom is 4-coordinate, binding to the less hindered distal nitrogens of the pyrazines of two separate ligands and two iodine atoms, and has a tetrahedral coordination geometry. The copper atoms are bridged by two iodine atoms to form a Cu_2I_2 square motif. Figure 2.67 depicts the connectivity of the complex and also the bridging copper iodide square motif. This Cu_2I_2 square motif is quite common for copper iodide complexes. The distance between the copper atoms in the square motif is 2.672Å. This intermetallic distance is shorter than that of the sum of the van der Waals radii of two copper(I) atoms (2.80Å), although the copper atoms are unlikely to form a real intermetallic bond.[183, 184] The Cu-N bond lengths are 2.022Å and 2.048Å, which are similar to related bond lengths in this thesis. The Cu-I bond lengths are 2.675Å and 2.626Å which are similar to other compounds with similar Cu_2I_2 motifs. Each copper atom coordinates to two separate ligand nitrogens and, since there are two copper atoms in each of the square motifs, each Cu_2I_2 square coordinates to four separate ligands. The resulting complex is a 'necklace' type polymer, which is a one-dimensional polymeric chain made up of M_4L_2 macrocyclic units linked by Cu_2I_2 squares. The topology of the necklace complex is clearly depicted in figure 2.68.

Each macrocyclic unit is composed of two ligands that are coordinated to two copper iodide squares resulting in a M_4L_2 macrocycle. The two halves of the macrocyclic unit are related by a two-fold rotation axis. Each M_4L_2 macrocyclic unit has a square topology, with the quaternary carbon atoms of two ligands forming two corners of the square and the copper iodide squares forming the other two corners of the square. The dimensions of the square can be described by the length of the sides, with dimensions of 10.761Å x 10.812Å. There is quite a large space inside each of the macrocyclic squares;

however there is no indication of any significant interactions with solvent or guest molecules.

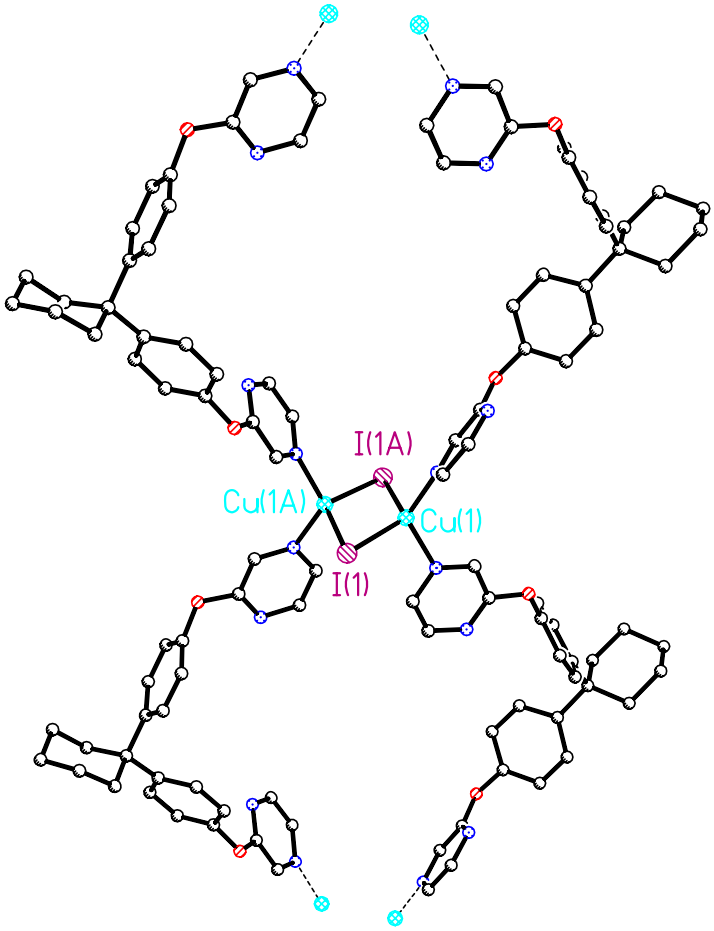


Figure 2.67 - *Perspective view illustrating the connectivity of complex* ***2.65*** *and the* Cu_2I_2 *square motif.*

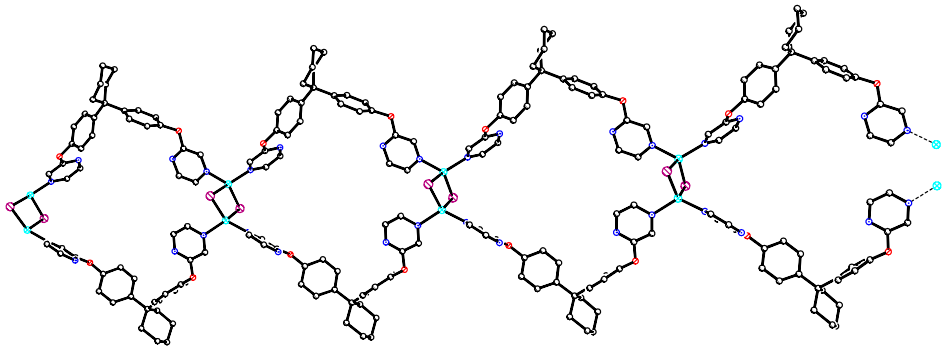


Figure 2.68 – *A section of the 'necklace' polymer* ***2.65***.

The M_4L_2 macrocyclic units propagate in one-dimension, forming a chain of inter-linked squares. Each of the M_4L_2 macrocycles is inter-linked by bridging copper iodide motifs that lie perpendicular to the joining macrocycles. The overall topology of the complex is that of a necklace topology with a continuous chain of big rings (the M_4L_2 macrocycles) inter-linked by smaller rings (the Cu_2I_2 squares). However, this necklace topology is quite different to that seen in the previously discussed copper chloride complexes **2.37** and **2.62**.

In the crystal packing the necklace chains pack with numerous hydrogen bonding interactions between them. There are no π-π stacking interactions between aromatic rings within a macrocyclic unit, because of the conformation and orientation of the ligands and the size of the M_4L_2 square macrocycle units. The necklace chains stack on top of each other with edge-to face π interactions between the benzene rings and pyrazine rings (2.804Å) of adjacent strands. The iodine atoms interact with the hydrogen atoms of pyrazine rings on other strands with the shortest interaction being 3.109Å.

*Crystal structure of the complex with $CoBr_2$ (**2.66**)*

Ligand **2.54** and cobalt(II) bromide were both dissolved in acetone and the solutions combined. Blue plate-like crystals formed overnight in the reaction mixture which were suitable for X-ray crystallography. The complex crystallises in the centrosymmetric monoclinic space group C2/c with one ligand molecule, one cobalt atom and one bromide counterion in the asymmetric unit. The asymmetric unit of complex **2.66** with its connectivity shown is depicted in figure 2.69 with the hydrogens removed for clarity. X-ray analysis revealed another necklace type complex, but with quite a different topology to the copper iodide necklace complex **2.65**.

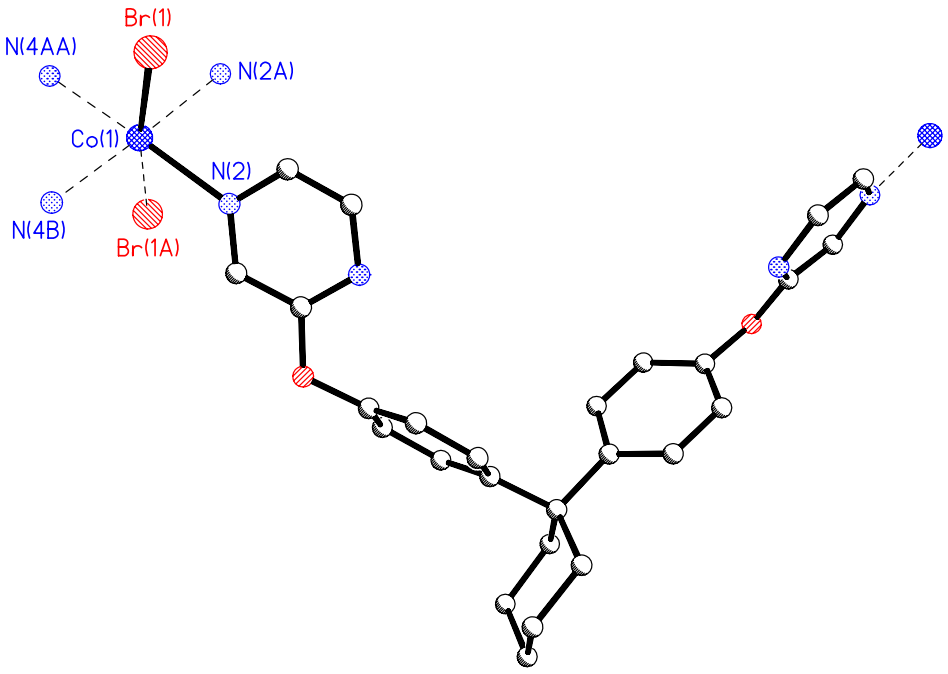


Figure 2.69 – *Contents of the asymmetric unit of complex* ***2.66****. Selected bond lengths (Å) and bond angles (°): Co1-N4B 2.231(2), Co1-N2 2.250(2), Co1-Br1 2.562(2), N2-Co1-N2A 87.98(8), N2-Co1-Br1 87.01(4), N2-Co1-Br1A 87.23(4), N2A-Co1-Br1A 87.01(4), N2B-Co1-Br1A 87.23(4), N4B-Co1-N4AA 83.89(8), N4B-Co1-N2 94.07(6), N4B-Co1-N2A 177.96(6), N4B-Co1-Br1 93.11(4), N4B-Co1-Br1A 92.84(4), Br- Co1-Br1A 171.99(2).*

Once again the conformation of the ligand in complex **2.66** is similar to the conformation of the ligand itself in the solid state. The cyclohexane ring is in a locked conformation with the two benzene rings in the axial and equatorial positions about the central quaternary carbon. The ligand has a concave shape and has a similar 'V-type' arrangement with the two aromatic benzene groups acting as the arms of the 'V' linked via the central quaternary carbon atom. The pyrazine rings are perpendicular to the attached benzene rings with the internal nitrogen atoms twisted to point inwards towards the centre of the cavity between the two benzene rings and the distal nitrogens are pointing outwards in order to bind to the cobalt atoms.

Each of the cobalt atoms has an elongated octahedral geometry coordinating to four separate pyrazine nitrogens and two bromine atoms. As expected the cobalt atom coordinates through the less hindered nitrogen atom of the pyrazine group. The basal plane is occupied by four nitrogen atoms from separate ligands and the two apical

positions are occupied by the two bromine atoms. Each ligand molecule coordinates to two separate cobalt atoms that act as a bridge between ligand molecules and a co-bridging ligand molecule is related by a two fold-rotation axis that passes through the cobalt atoms. The resulting complex is a 'necklace' type polymer composed of M_2L_2 macrocyclic units that are linked by octahedral cobalt atoms. The topology of this 'necklace' complex is clearly depicted in figure 2.70. The Co-N bond distances are 2.250Å (Co1-N2) and 2.231Å (Co1-N4B) and the Co-Br bond lengths are 2.562Å, which are within the same range as related complexes.[185]

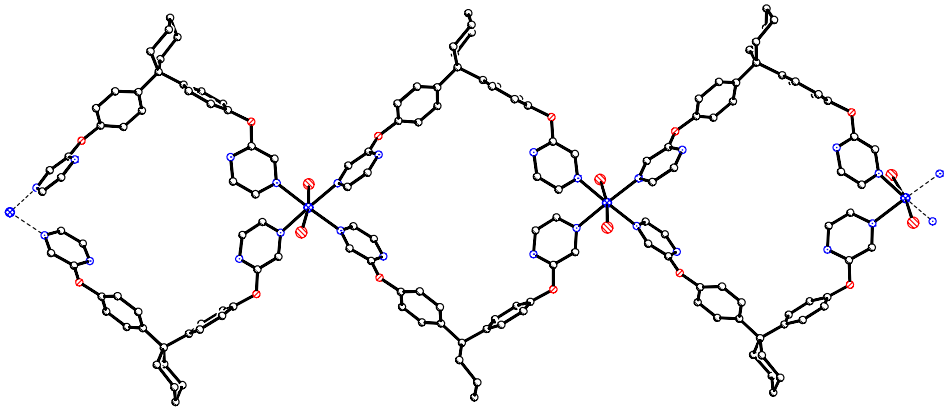


Figure 2.70 – *A section of the one-dimensional necklace polymer composed of square M_2L_2 macrocyclic units joined by cobalt atoms.*

Two ligands are coordinated to two cobalt atoms to form a M_2L_2 macrocycle. Each of the macrocyclic units has a similar square topology to that seen in the copper complex **2.65**, with the quaternary carbon atoms of two ligands forming two corners of the square and the cobalt atoms forming the other two corners of the square. The distance between the two quaternary carbon atoms across the squares is 14.913Å and the distance between cobalt atoms across the square is 16.151Å. This square has similar dimensions to the M_4L_2 squares seen in complex **2.65**. There is also a large void inside each of the M_2L_2 squares; however there are no host guest interactions inside the cavity. Effectively the cobalt atoms act as spiro centers that link together two square units.

The overall necklace topology is quite different to previously reported necklace complexes in this thesis. Instead of having a continuous chain of big rings inter-linked by smaller rings, complex **2.66** has a chain of the same sized rings linked together via single atoms. This type of necklace topology is quite common in the field of

metallosupramolecular chemistry and many coordination complexes of a similar nature have been made. To the best of our knowledge there are only a few reported cobalt bromide coordination complexes with octahedral cobalt atoms bound to four nitrogen containing heterocycles and two bromine atoms. In fact the *Crystallographic Structural database* (Version 1.10, March 2008) revealed only a handful of such cobalt bromide complexes with octahedral cobalt atoms linked to nitrogen containing heterocycles.[185-188] None of the reported octahedral cobalt bromide complexes yielded any necklace type polymers and no cobalt bromide complexes with pyrazine ligands are in the literature. Therefore, to the best of our knowledge this is the first reported cobalt bromide necklace polymer with octahedral cobalt centers and pyrazine ligands.

In the packing of **2.66** the one-dimensional chains stack on top of each other with each chain offset from adjacent chains. Necklace chains stack with a few significant interactions between ligands. The ligands stack via edge-to-face interactions between pyrazine rings and benzene rings of adjacent necklace strands with distances of 2.568Å and 2.612Å. There are also some close hydrogen bonding interactions between ligand molecules and bromine atoms of adjacent necklace strands that range between 2.647Å and 3.040Å.

*Other complexes with ligand **2.54***

Ligand **2.54** was reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgCF_3SO_3$, $AgBF_4$, $AgClO_4$, $PdCl_2$, $PdCl_2(PhCN)_2$, $ZnBr_2$ and $ZnCl_2$. Complexation of ligand **2.54** with the metals salts $CoBr_2$ and CuI gave crystals suitable for X-ray crystallography, which have already been discussed. Unfortunately, X-ray quality crystals or crystalline solids were not formed with all of these metal salts. Some of the complexes gave precipitates immediately, however despite several attempts most of these complexes could not be recrystallised and were not analysed any further.

Reaction of ligand **2.54** with $CuCl_2$ produced a green crystalline solid on slow evaporation. Elemental analysis revealed a complex with a 2:1 M:L ratio. This 2:1 ratio suggests the possible formation of a discrete complex or perhaps a polymeric complex. A polymeric complex could be made from ligands that are linked together by some

Cu_2Cl_4 squares, similar to the copper iodide complex **2.65** with the Cu_2I_2 squares. The formation of such interesting copper chloride motifs or squares has been explored a couple of times so far in this thesis with complexes of other ligands.

Ligand **2.54** was reacted with $AgPF_6$, $AgCF_3SO_3$ and $AgClO_4$ and formed white precipitates immediately after mixing. These white precipitates were analysed by elemental analyses and revealed 1:1 metal to ligand ratios with similar melting points. The two complexes **2.65** and **2.66** formed necklace type polymers and analysed with a 1:1 ratio of metal to ligand. Therefore, it is likely that ligand **2.54** could form similar necklace type polymers with these silver salts as well.

Complexes with ligands 2.55 and 2.56

Ligands **2.55** and **2.56** were reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgCF_3SO_3$, $AgBF_4$, $AgClO_4$, $PdCl_2$, $PdCl_2(PhCN)_2$, $ZnBr_2$ and $ZnCl_2$. Unfortunately, despite several attempts, no crystals suitable for X-ray crystallography were obtained for either of the ligands. Complexation of both ligands **2.55** and **2.56** mostly gave precipitates or crystalline solids. On some occasions X-ray quality crystals were grown for either the free ligand or the starting metal salt. For example, crystals of ligand **2.56** were grown from a complex solution of $ZnCl_2$ with ligand **2.56**. Attempts were made to recrystallise some of the precipitates, however these were unsuccessful and most of the complexes were not analysed any further.

Reaction of ligand **2.55** with $CuCl_2$ produced a green crystalline solid on slow evaporation. Elemental analysis revealed a complex with a 2:1 ratio of metal to ligand.

Elemental analyses were carried out on some of the silver complexes made with ligand **2.55**. Ligand **2.55** was reacted with $AgPF_6$, $AgClO_4$ and $AgBF_4$ to give colourless crystalline solids with $AgPF_6$ and $AgBF_4$ and a brown precipitate with $AgClO_4$. The complexes formed with $AgClO_4$ and $AgBF_4$ analysed with a 1:1 ratio of metal to ligand, whereas the complex formed with $AgPF_6$ revealed an unusual M_4L_3 complex. A structure containing this unusual ratio of metal to ligand is possible and suggests quite an intricate structure. On the other hand there could be a mixture of products in the one

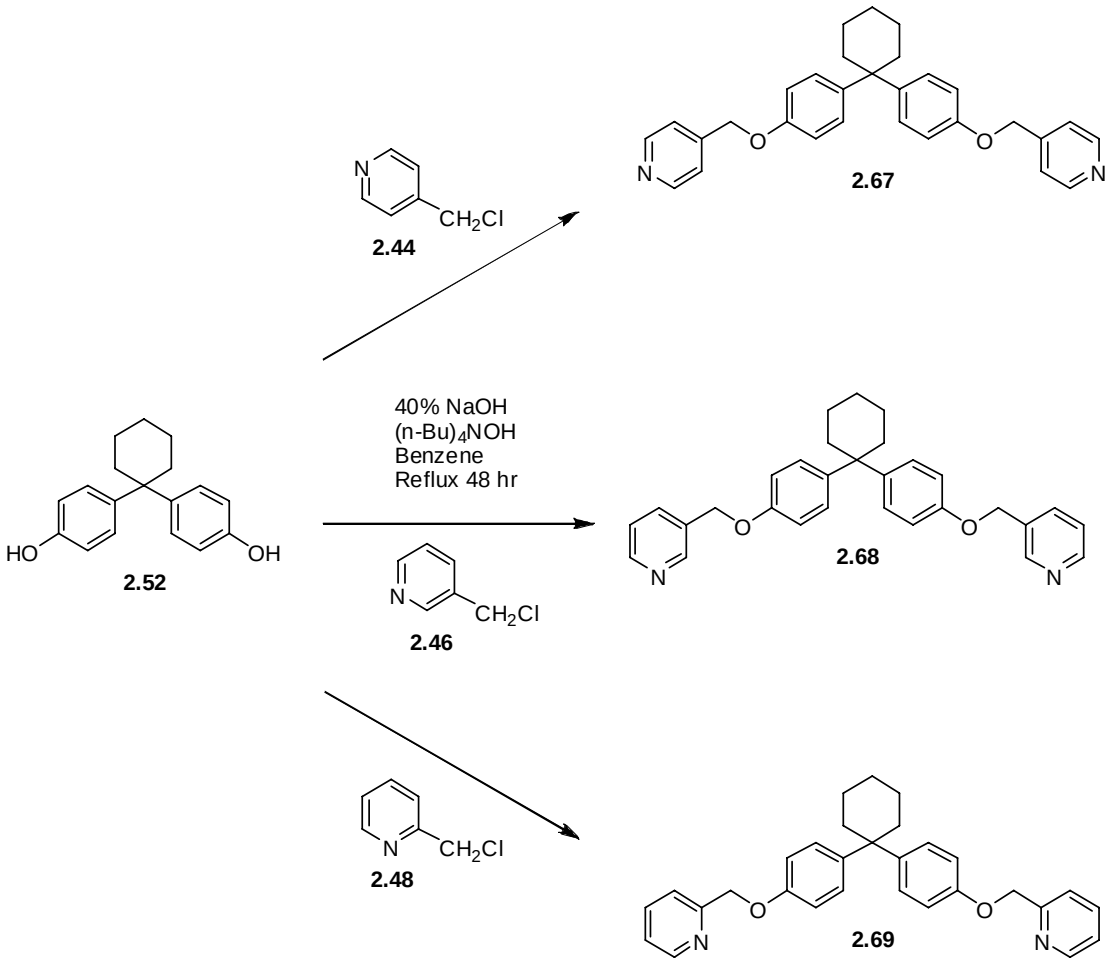
sample and therefore the sample analysed may not be representative of the whole sample.

Elemental analyses were carried out on some of the silver complexes made with ligand **2.56**. Ligand **2.56** was reacted with $AgPF_6$, $AgClO_4$ and $AgBF_4$ and yellow solids were formed with all three mixtures within minutes of mixing. Two of the complexes ($AgPF_6$ and $AgClO_4$) analysed with 1:1 ratios, which suggests the formation of a discrete complex or some kind of polymeric complex. The $AgBF_4$ complex analysed as a M_2L complex. Since the ligand has the ability to bind four metal atoms, the M_2L ratio suggests the possible formation of a discrete complex, or interesting polymeric complex with M_2L units that could be linked by bridging anions and/or solvent molecules.

Synthesis of the Bisphenol Z based -CH_2O- spaced ligands

Finally, three more ligands were synthesised from the Bisphenol Z core, this time with a spacer group containing two atoms, instead of just one. The spacer group was extended by use of a methyleneoxy (-CH_2O-) group between the benzene ring and a 2-, 3- or 4-substituted pyridine ring. Overall, these compounds are very similar to ligand **2.53**, but with an extra CH_2 spacer group.

The final three Bisphenol Z ligands **2.67**, **2.68** and **2.69** were synthesised by phase-transfer-catalysed (PTC) reactions, as previously used with the Bisphenol A backboned ligands. The method adopted was analogous to that of Hartshorn et al.[102, 172] The PTC method has proved to be very successful and has generated many other structurally related ligands in the Steel group over the years. The new Bisphenol Z backboned ligands with a methyleneoxy spacer group are shown in Scheme 2.6. Phase-transfer-catalysed (PTC) double alkylation of bisphenol Z (**2.52**) with three isomeric chloromethylpyridines gave ligands **2.67**, **2.68** and **2.69** in low crude yields. Flash chromatography of ligand **2.67** gave a white crystalline solid in a modest yield of 14%. Ligands **2.68** and **2.69** were recrystallised from petroleum ether/ethyl acetate to generate an orange solid and a white solid respectively. Once again these ligands were isolated in modest yields of 16% (**2.68**) and 45% (**2.69**). Subsequently, these ligands were fully characterised by elemental analyses, mass spectrometry, melting points and by ^1H and ^{13}C NMR.[113]



Scheme 2.6 - *Synthesis of new ligands **2.67**, **2.68** and **2.69** with the Bisphenol Z backbone.*

Since one intends to use the new bridging ligands **2.67**, **2.68** and **2.69** as synthons to generate metallosupramolecular species, one is also interested in determining their solid state structures. Unfortunately no crystals were obtained of just the ligands themselves.

Complexes with ligand 2.67

Complexation of ligand **2.67** was attempted with only a selection of metal salts, due to the low isolated yield of the product. Ligand **2.67** was reacted with $CoBr_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $ZnBr_2$, $AgPF_6$, $AgCF_3SO_3$ and $AgClO_4$. All of these reactions formed precipitate solids that that were insoluble in most common solvents. Therefore, none of these complexes would be recrystallised.

When $CoBr_2$ was reacted with **2.67** a blue crystalline solid was generated that analysed with a 1:1 ratio. This could suggest the formation of a discrete structure, such as a square dimer, or a coordination polymer. Reaction of **2.67** with $AgPF_6$ and $AgClO_4$ gave crystalline precipitates immediately after mixing. Both these complexes analysed with 1:1 ratios suggesting the potential formation of a discrete species or coordination polymer. Ligand **2.67** with $ZnBr_2$ also analysed with a 1:1 stoichiometry suggesting the formation of similar products to that mentioned above.

Complexes with ligand 2.68

*Crystal structure of the complex with $ZnCl_2$ (**2.70**)*

Ligand **2.68** and zinc chloride were mixed together in solution. Over time a small amount of crystalline precipitate formed in the reaction mixture. Further examination of the crystalline precipitate under the microscope revealed a scattering of thin colourless plates amongst the precipitate. Unfortunately most of the plates were stacked on top of each other and were not easily broken apart. Despite this a few crystalline plates were fished out and put up for X-ray crystallographic analysis and a structure was obtained. However, the thin crystal plates were poor diffractors and due to disorder the final R_1 value was only 9.67%.

X-ray analysis revealed a [2+2] macrocycle that crystallises in the monoclinic space group $P2_1/c$. The asymmetric unit contains one whole ligand molecule, one $ZnCl_2$, one methanol solvate molecule and a disordered water molecule. The elemental analysis revealed the same 1:1 ratio of metal to ligand without the methanol solvent molecule. Figure 2.71 shows the whole [2+2] macrocycle, with the hydrogens and solvent molecules excluded for clarity. The two asymmetric units combine about a centre of inversion to give the [2+2] macrocycle, as depicted in figure 2.71. Overall, this is considered a 40-membered macrocycle, which is large, but is not the largest macrocycle discussed in this thesis. The Zn-N bond lengths are 2.041Å and 2.054Å, which are both within the range of other zinc chloride complexes discussed in this thesis. The Zn-Cl bond lengths are 2.230Å and 2.233Å and are also within the range of other zinc chloride complexes.[166-171]

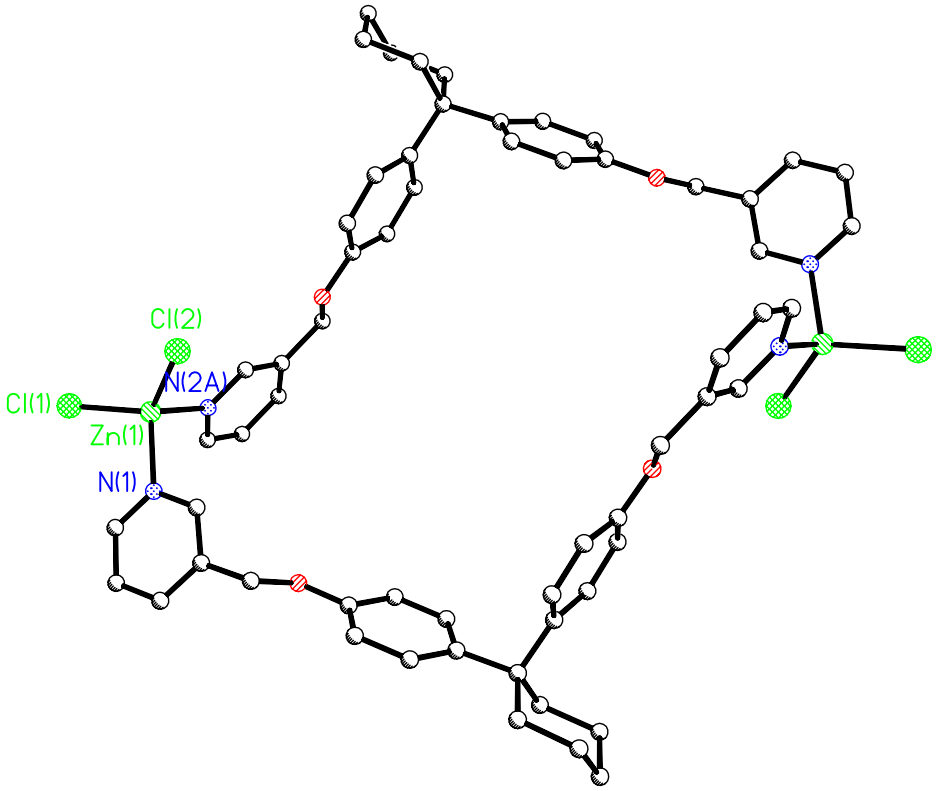


Figure 2.71 – *Perspective view of the [2+2] square macrocycle generated from ligand* **2.68** *and* $ZnCl_2$. *Selected bond lengths (Å) and bond angles (°): Zn1-N1 2.054(5), Zn1-N2A 2.040(4), Zn1-Cl1 2.233(2), Zn1-Cl2 2.230(2), N2A-Zn1-N1 106.1(2), N1-Zn1-Cl1 104.9(1), N1-Zn1-Cl2 110.1(1), N2A-Zn1-Cl1 107.8(1), N2A-Zn1-Cl2 105.7(2), Cl2-Zn1-Cl1 121.4(7).*

The zinc atoms are 4-coordinate, being bound to two nitrogen atoms of separate ligands and two chlorine atoms with a distorted tetrahedral geometry. The largest deviation from tetrahedral arises between the chlorine atoms with an angle of 121.4°. The cyclohexane ring is locked in a conformation with the two ligand arms in the axial and equatorial positions about the quaternary carbon. On the arms of the ligand, one of the pyridine rings is almost perpendicular to the attached benzene ring, with the nitrogen atom pointing downwards in order to coordinate to the zinc metal atom. The other arm of the ligand adopts an *anti* conformation with the pyridine ring almost coplanar with the attached benzene ring and the nitrogen atom pointing outwards away from the center of the ligand.

The conformation of the ligand in complex **2.70** is ideal for the formation of quite a symmetrical [2+2] macrocycle. The [2+2] macrocycle has a square shape with the

corners of the square defined by the two zinc atoms and the two quaternary carbon atoms of the ligands. The macrocycle does not form a perfect square and is more realistically described as rectangular in shape. The distance between the two zinc atoms across the diagonal is 16.352Å and the distance between the two quaternary carbon atoms on the other diagonal is 14.292Å. As one can see there is quite a large cavity inside the macrocycle. However, despite the size of the cavity there are no significant host guest type interactions especially since the methanol solvent molecule is sitting outside the square. Also there are no π-π stacking interactions between aromatic rings within a square, because of the large size of the [2+2] macrocycle. Even though the benzene rings and pyridine rings are almost aligned on opposing sides of the square, the distance is far too great for π-π stacking interactions (11.255Å) to occur.

In the crystal packing the methanol and water solvent molecules interact extensively with the macrocycles through various hydrogen bonding interactions filling up voids in the crystal lattice. The macrocycles pack with a few hydrogen bonding interactions between adjacent macrocyclic dimers, but no significant π-π stacking or edge-to face π interactions occur due to the alignment and orientation of the macrocyclic units in the extended structure.

*Other complexes with ligand **2.68***

Complexation of ligand **2.68** was attempted with only a few metal salts, due to only a small amount of product being isolated. Ligand **2.68** was reacted with $CuCl_2$, CuI, $Cu(NO_3)_2$, $ZnCl_2$, $ZnBr_2$, $AgPF_6$, $AgCF_3SO_3$ and $AgClO_4$. Reaction of ligand **2.68** with $ZnCl_2$ gave a solid that had some crystals scattered throughout the solid that were able to be fully characterised by X-ray analysis. Unfortunately, this was the only complex to be fully characterised with ligand **2.68** and the rest of the complexes gave precipitates. Attempts were made to recrystallise these precipitates, however they were insoluble in most common solvents.

Crystalline precipitates formed immediately on reaction of ligand **2.68** with silver salts $AgPF_6$ and $AgClO_4$ and both analysed with a 1:1 ratio. This ratio suggests the possible formation of a discrete species, such as a [2+2] macrocycle generated with $ZnCl_2$ (**2.70**), or a coordination polymer. A $ZnBr_2$ complex also analysed with a 1:1 ratio. In this case

a [2+2] macrocycle is the most likely product, because ligand **2.68** formed a [2+2] macrocycle with $ZnCl_2$.

Complexes with ligand 2.69

*Crystal structure of the complex with CuI (**2.71**)*

Slow evaporation of a solution containing ligand **2.69** and copper(I) iodide produced pale yellow plate-like crystals that were suitable for X-ray crystallography. The structure crystallises in the triclinic space group P-1, with one ligand molecule, one copper iodide and a disordered dichloromethane molecule in the asymmetric unit. The contents of the asymmetric unit are shown in figure 2.72, with the hydrogens and dichloromethane solvent molecule omitted for clarity. The structure contains a dichloromethane molecule that is disordered over two sites, although the residual electron density map suggests the disorder may be more extensive than this.

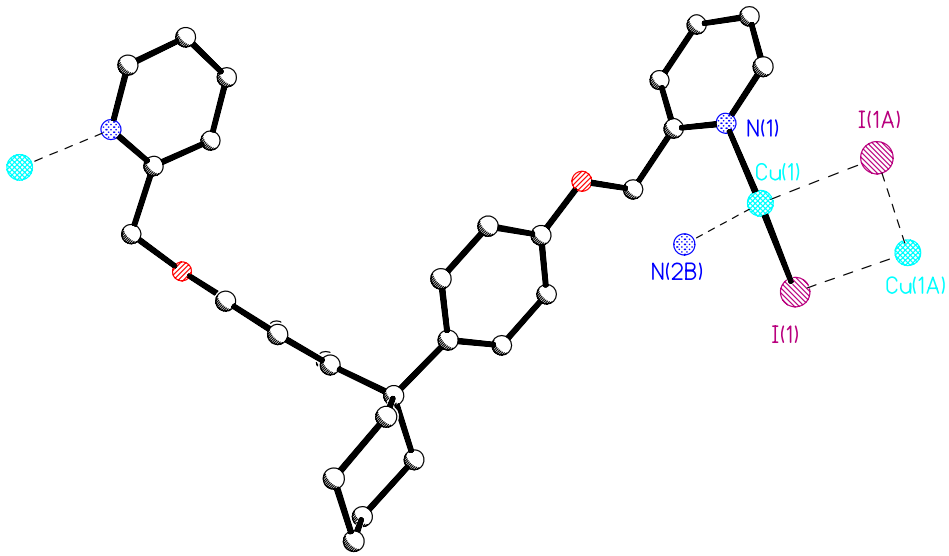


Figure 2.72 – *Contents of the asymmetric unit of complex **2.71**. Selected bond lengths (Å) and bond angles (°): I1A-Cu1 2.6654(7), I1-Cu1 2.6697(7), Cu1-N2B 2.053(4), Cu1-N1 2.089(4), Cu1-I1-Cu1A 69.23(2), N2B-Cu1-N1 113.9(2), N2B-Cu1-I1A 110.4(1), N1-Cu1-I1A 107.6(1), N2B-Cu1-I1 110.9(1), N1-Cu1-I1 103.1(1), I1-Cu1-I1A 110.77(2).*

In complex **2.71** the two benzene rings and the cyclohexane ring twist around the central quaternary carbon of the Bisphenol Z backbone in a propeller type arrangement.

The cyclohexane ring is in a locked chair conformation with one benzene ring in the equatorial position and one in the axial position. One of the ligand binding arms is extended out in an *anti* conformation, with the pyridine ring almost perpendicular to the attached benzene ring and the nitrogen atom pointing outwards in order to coordinate to the copper atom. The other binding arm of the ligand adopts a *gauche* conformation with the nitrogen atom also pointing outwards. Therefore the two pyridine nitrogens are pointing away from one another.

The copper atoms are 4-coordinate, binding to two pyridine nitrogens from two separate ligands and two iodine atoms with a distorted tetrahedral geometry. The largest deviation from tetrahedral is seen in the bond angle 103.1° (N1-Cu1-I1). The copper atoms are bridged by two iodine atoms to give a planar Cu_2I_2 square. This Cu_2I_2 square motif is not uncommon in copper iodide complexes. In fact another copper iodide complex with a Cu_2I_2 square has already been discussed in complex **2.65**. Complex **2.71** is a necklace type structure composed of M_2L_2 macrocyclic units of the pyrazine substituted Bisphenol Z ligand linked by Cu_2I_2 squares. The distance between copper atoms in a square motif is 3.031Å. This distance is longer than that of the sum of the van der Waals radii of two copper(I) atoms (2.80Å)[183, 184] and suggests that the interaction between the two copper atoms in a square is relatively weak. A view of the Cu_2I_2 motif is more clearly shown in figure 2.73. The Cu-N bond lengths are 2.053Å and 2.089Å and the Cu-I bond lengths are 2.665Å and 2.670Å, which are within the range of other copper iodide complexes with Cu_2I_2 motifs. Each copper atom coordinates to two separate pyridine nitrogens and since there are two copper atoms in each of the square motifs, each Cu_2I_2 square motif coordinates to four separate ligands. The resulting complex is a 'necklace' type polymer, which is a 1-dimensional polymeric chain composed of M_2L_2 macrocyclic units linked by planar Cu_2I_2 squares. The topology of the necklace complex is clearly depicted in figure 2.74.

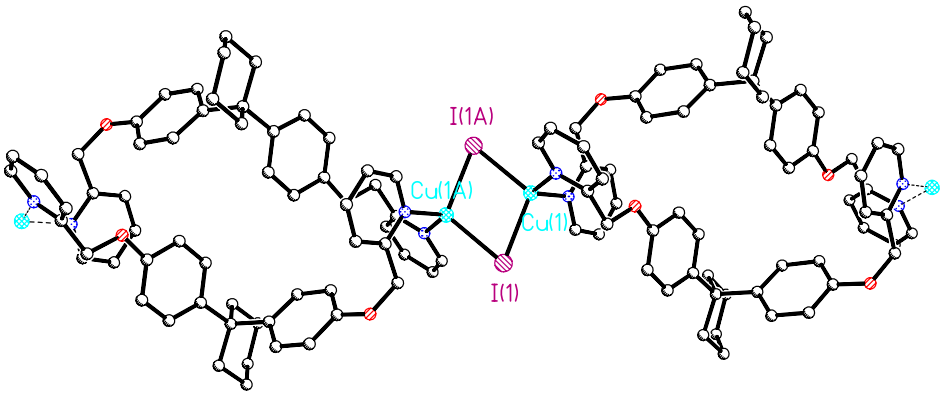


Figure 2.73 – *View of complex* ***2.71*** *illustrating the Cu_2I_2 square motif and the weak intermetallic interaction between the two copper atoms.*

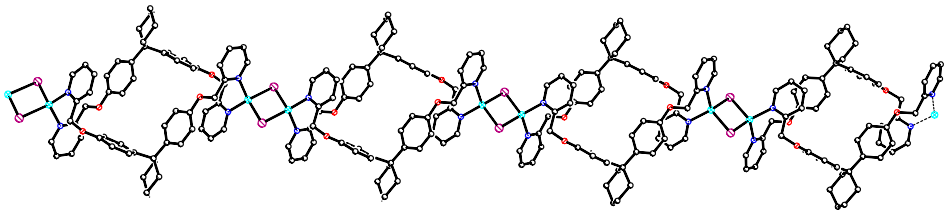


Figure 2.74 – *A section of the one-dimensional 'necklace' type polymer* ***2.71***.

A macrocyclic unit is made up of two ligand molecules bound to two Cu_2I_2 squares. The Cu_2I_2 squares lie on centers of inversion to generate the overall complex 'necklace' topology. This 'necklace' type polymer has a similar topology to the copper iodide complex **2.65** and copper chloride complexes **2.37** and **2.62**, all of which had 'necklace' type structures. Due to the conformation of the ligand and the way the pyridine rings twist around to bind to the Cu_2I_2 squares, each ligand overlaps the other ligand within a M_2L_2 macrocycle. This overlapping of ligands is seen more clearly in figure 2.74 and also reduces the space in the cavity of the macrocycle. The dichloromethane solvent molecule also does not interact inside the cavity. However, there are some favourable π-π stacking interactions between benzene rings and pyridine rings (3.359Å) within a macrocycle, which are close to that of the value found in graphite (3.35Å).[9, 10, 12] There are also some weaker edge-to-face interactions between benzene rings (2.635Å) within a macrocycle.

The 'necklace' polymer propagates in one-dimension, with M_2L_2 macrocycles inter-linked by Cu_2I_2 squares. Each of the M_2L_2 macrocycles is inter-linked by bridging Cu_2I_2 motifs that lie perpendicular to the adjoining macrocycles. The overall topology of the structure is a continuous chain of large rings (the M_2L_2 macrocycles) inter-linked by smaller rings (the Cu_2I_2 squares).

In the crystal packing the necklace chains pack with numerous hydrogen bonding interactions between them. The dichloromethane solvent molecule interacts extensively in the structure and fills voids in the crystal lattice. The necklace chains stack with various hydrogen bonding interactions between ligand molecules of adjacent necklace strands. The iodine atoms interact with the dichloromethane solvent molecules and methylene hydrogen atoms of the ligands (3.062Å).

*Crystal structure of the complex with $Cu(NO_3)_2$ (**2.72**)*

Crystals of complex **2.72**, suitable for X-ray crystallography were obtained by layering a methanol solution of copper nitrate upon a solution of ligand **2.69** in dichloromethane. After a week single blue crystals of complex **2.72** formed. The copper nitrate complex crystallises in the monoclinic space group $P2_1/n$ and reveals an intricate one-dimensional polymeric structure. The asymmetric unit contains one ligand molecule, two copper atoms, two nitrate anions, two methoxide anions and partially occupied dichloromethane and methanol solvent molecules. The structure proved to be a 2:1 metal to ligand complex, in which both the copper atoms are 5-coordinate, as shown by the asymmetric unit in figure 2.75. In complex **2.72**, the cyclohexane ring is in a locked chair conformation with one benzene ring in the equatorial position and one in the axial position. Both of the ligand binding arms are extended out in an *anti* conformation, with the pyridine ring almost coplanar to the attached benzene ring and the nitrogen atom pointing outwards. The *anti* conformation of the ligand is ideal to allow the ligand to be able to chelate to both the nitrogen and oxygen atoms of the ligand.

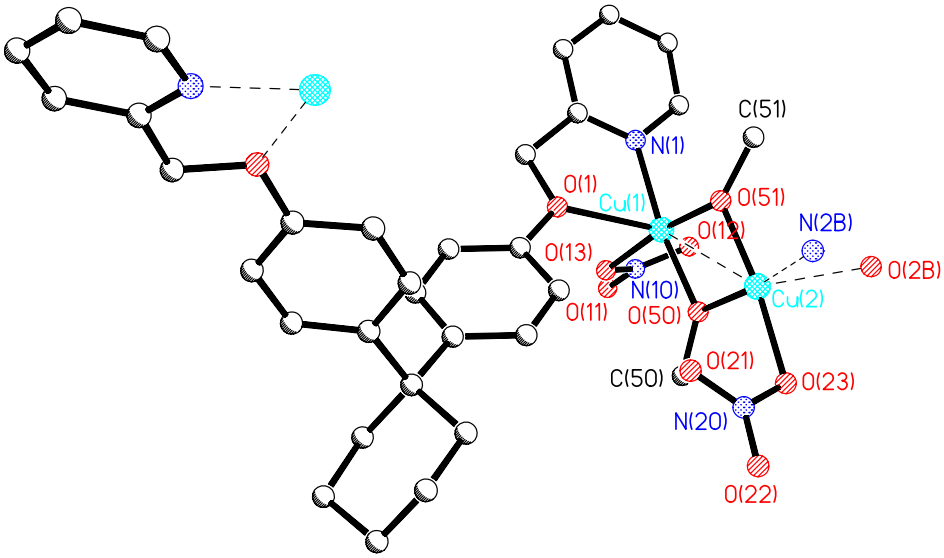


Figure 2.75 – *Contents of the asymmetric unit of complex* ***2.72****. Selected bond lengths (Å) and bond angles (°): Cu1-O50 1.912(2), Cu1-O51 1.945(2), Cu1-N1 2.002(2), Cu1-O13 2.006(2), Cu1-O1 2.369(2), Cu1-Cu2 3.0176(6), Cu2-O51 1.921(2), Cu2-O50 1.928(2), Cu2-O23 1.991(2), Cu2-N2B 2.015(2), Cu2-O2B 2.387(2), O50-Cu1-O51 76.76(8), O50-Cu1-N1 172.16(9), O51-Cu1- N1 96.46(9), O50-Cu1-O13 95.24(8), O51-Cu1-O13 171.88(8), N1-Cu1-O13 91.62(9), O50-Cu1-O1 110.12(8), O51-Cu1-O1 96.94(9), N1-Cu1-O1 74.29(9), O13-Cu1-O1 84.43(9), O51-Cu2-O50 76.96(8), O51-Cu2-O23 172.56(9), O50-Cu2-O23 95.97(8), O51-Cu2-N2B 98.41(9), O50-Cu2-N2B 172.66(9), O23-Cu2-N2B 88.38(9), O51-Cu2-O2B 95.52(8), O50-Cu2-O2B 110.81(8), O23-Cu2-O2B 89.11(8), N2B-Cu2-O2B 75.08(9).*

Both of the copper atoms are 5-coordinate with distorted square pyramidal geometry. Both copper atoms are coordinated to one nitrogen atom and one oxygen atom of the ligand, one oxygen atom of a nitrate anion and two methoxide oxygens. Each copper atom is chelated to the ligand through the nitrogen and oxygen atoms and is also coordinated to a monodentate nitrate anion. Each copper atom is also further bridged by two methoxide groups to another copper atom, resulting in a planar dinuclear copper(II) methoxide bridged square motif. This type of copper(II) methoxide bridging motif is relatively uncommon and there are only a few examples of this motif reported in the literature.[189-192] The distance between copper atoms in the square is 3.018Å, which is similar to the interatomic distance found in structurally related examples.[189-192] The basal plane for both copper(II) centers is composed of a pyridine nitrogen atom, the monodentate nitrate anion and the two bridging methoxide oxygen atoms. The copper centers are almost symmetric with the apical site occupied by the chelating oxygen

atom of the ligand with a bond distance of 2.369Å for Cu1 and 2.387Å for Cu2. The distance between copper centers and the bridging methoxide oxygen atoms range between 1.912Å-1.945Å, which are similar to other related methoxide bridging copper(II) complexes. The Cu-N distances are also all within the range of other related methoxide bridging copper(II) complexes.[189-192] The monodentate nitrate anions coordinate to each of the copper atoms through one oxygen atom with Cu-O bond lengths of 1.991Å for Cu2 and 2.006Å for Cu1. Once again these values lie within the literature range for monodentate nitrate anions coordinated to copper(II) atoms.

The resulting complex is an undulating one-dimensional polymer composed of ligand molecules linked to methoxide bridging copper(II) squares. Each ligand is bridged by two copper(II) methoxide bridging square motifs related by a two-fold screw axis. The one-dimensional chain has a continuous alternating orientation of the ligands between the methoxide bridged copper(II) squares, so that each copper(II) motif is coordinated to a ligand above and below it. A section of the one-dimensional polymer chain is depicted in figure 2.76.

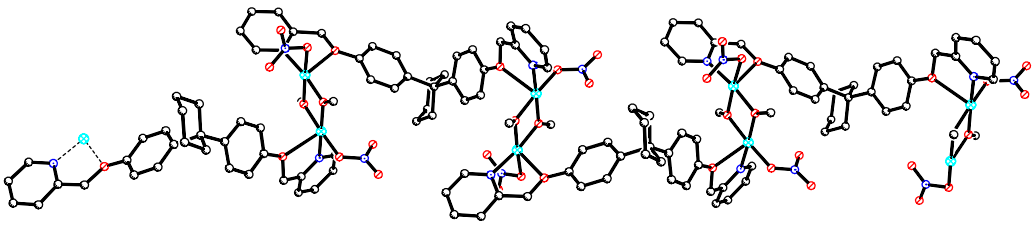


Figure 2.76 – *A section of the undulating one-dimensional polymer* ***2.72*** *with the methoxide bridged copper(II) square motifs.*

In the packing of complex **2.72** the dichloromethane and methanol solvent molecules interact extensively with the copper polymer chains and nitrate counterions through various hydrogen bonding interactions. The polymer chains interact with only a few other significant interactions, such as C-H···π bonding between a hydrogen atom of the methyl group and the neighbouring pyridine ring (2.607Å). The oxygen atoms of the coordinated monodentate nitrate counterions are also involved in some C-H···O interactions with hydrogens from the ligand, with distances ranging between 2.292Å-2.715Å.

*Crystal structure of the complex with $ZnBr_2$ (**2.73**)*

Crystals of complex **2.73**, suitable for X-ray crystallography, were obtained by layering a methanol solution of zinc bromide upon a solution of ligand **2.69** in dichloromethane. Slow evaporation of the reaction mixture over time produced colourless crystals of **2.73**. The zinc bromide complex crystallises in the monoclinic space group $P2_1/c$ and reveals a one-dimensional helical polymeric structure. The asymmetric unit has one whole ligand molecule, one zinc metal atom and two bromine atoms. Figure 2.77 shows a small section of the polymer, with the hydrogen atoms omitted for clarity.

The helical topology shown in complex **2.73** is similar to that seen in many of the one-dimensional coordination polymers generated from the Bisphenol A derived ligand **2.19**. The topology is also similar to the one-dimensional helical coordination polymers constructed from the Bisphenol Z derived ligand **2.53**. The overall topology of all these complexes is very similar with the only real difference between the zinc complex **2.73** and other previously described helical complexes is the addition of a spacer group containing two atoms instead of just one in the ligand. Apart from this all of the one-dimensional helical coordination polymers are topologically very similar.

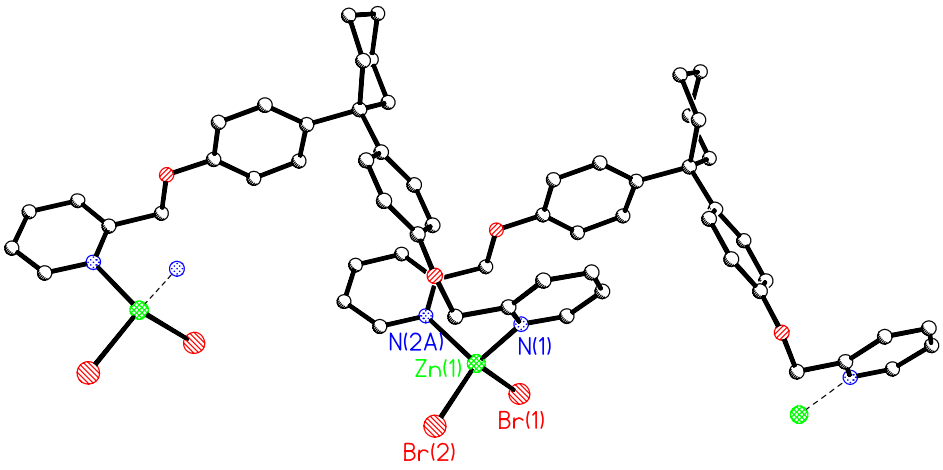


Figure 2.77 – *A small section of the one-dimensional helical polymer **2.73**. The complex is grown to show the overall connectivity of the structure. Selected bond lengths (Å) and bond angles(°): Zn1-N1 2.080(2), Zn1-N2A 2.124(2), Zn1-Br1 2.373(5), Zn1-Br2 2.360(5), N1-Zn1-N2A 107.43(9), N1-Zn1-Br1 111.04(7), N1-Zn1-Br2 110.29(7), N2A-Zn1-Br1 107.82(7), N2A-Zn1-Br2 108.75(7), Br2-Zn1-Br1 111.4(2).*

In the zinc bromide complex **2.73** the conformation of the ligand is similar to that seen in previous complexes. The cyclohexane ring is in a locked position with one benzene ring in the equatorial position and one in the axial position. One of the binding arms of the ligand is extended out, with the pyridine ring perpendicular to the attached benzene ring and the nitrogen atom pointing inwards towards the centre of the cavity between the two benzene rings. The other binding arm of the ligand adopts a *gauche* conformation with the nitrogen atom pointing outwards away from the central cavity of the ligand. This conformation of the ligand is ideal to allow the ligand to wrap around the zinc atoms in a helical fashion.

The zinc atom coordinates to two pyridine nitrogens and two bromine atoms with a distorted tetrahedral geometry. The largest deviation from the idealised tetrahedral geometry arises between the bromine atoms with an angle of 111.4°. The Zn-N bond lengths are 2.080Å and 2.124Å and the Zn-Br bond lengths are 2.373Å and 2.360Å, which are similar to the bond lengths of other helical zinc complexes reported so far in this thesis.

One-dimensional helical strands of complex **2.73** propagate down the a-axis of the unit cell by translation. Figure 2.78 depicts a larger section of the helical coordination polymer, with the hydrogens removed for clarity. The complex crystallises in a centrosymmetric space group, therefore both the P(right-handed) and M(left-handed) helices are present in the structure. The ligands twist and wrap around the zinc atoms to give a helical pitch of 9.429Å, which is equal to the length of the a-edge of the unit cell and corresponds to the distance between adjacent zinc atoms along the polymer strand. The pitch distance in complex **2.73** is a lot shorter than that of zinc helical polymers made from Bisphenol A (**2.42** and **2.43**) and Bisphenol Z (**2.63** and **2.64**). This may be because in complex **2.73** the ligand has one binding arm that adopts a *gauche* conformation, which enables the ligand to twist and wrap around the zinc atom in a helical fashion. As a result the ligand has a more compact structure, which thereby decreases the distance between zinc atoms in the helical polymer.

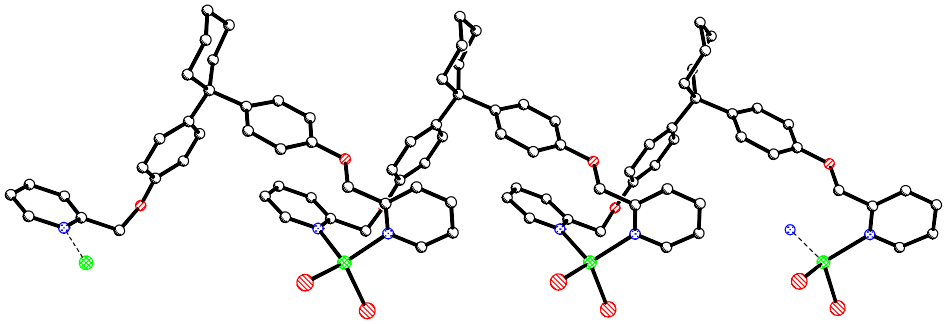


Figure 2.78 – *A larger section of the one-dimensional helical coordination polymer* ***2.73****, clearly illustrating the helical twist of the ligands around the zinc atoms.*

*Crystal structure of the complex with $ZnCl_2$ (**2.74**)*

A one-dimensional helical polymer was generated from reaction of zinc chloride and ligand **2.69**. Colourless plate-like crystals grew on the bottom of the vial and these were suitable for X-ray crystallography. The zinc chloride complex crystallises in the monoclinic space group $P2_1/c$ with one whole ligand molecule, one zinc atom and two chlorine atoms in the asymmetric unit. Figure 2.79 shows a section of the helical polymer, with the hydrogen atoms omitted for clarity. Surprisingly, the zinc chloride helical polymer has quite a different topology to the zinc bromide one-dimensional helical coordination polymer (**2.73**) described above. Complex **2.74** is composed of ligand/zinc strands that are more severely twisted along the helical axis. In fact this complex has a similar topology to the zinc bromide helical polymer **2.50** made with the 3-substituted methylpyridine derived from a Bisphenol A backbone discussed in the previous section.

In complex **2.74**, the cyclohexane ring is locked in a chair conformation with one benzene ring in the equatorial position and one in the axial position about central the quaternary carbon. One of the arms of the ligand is extended out in *anti* conformation with the pyridine ring and benzene ring almost coplanar to one another. The other binding arm of the ligand has a folded up *gauche* conformation. Both the nitrogen atoms on the ligand point outwards to wrap and twist around the zinc metal atom in a helical manner.

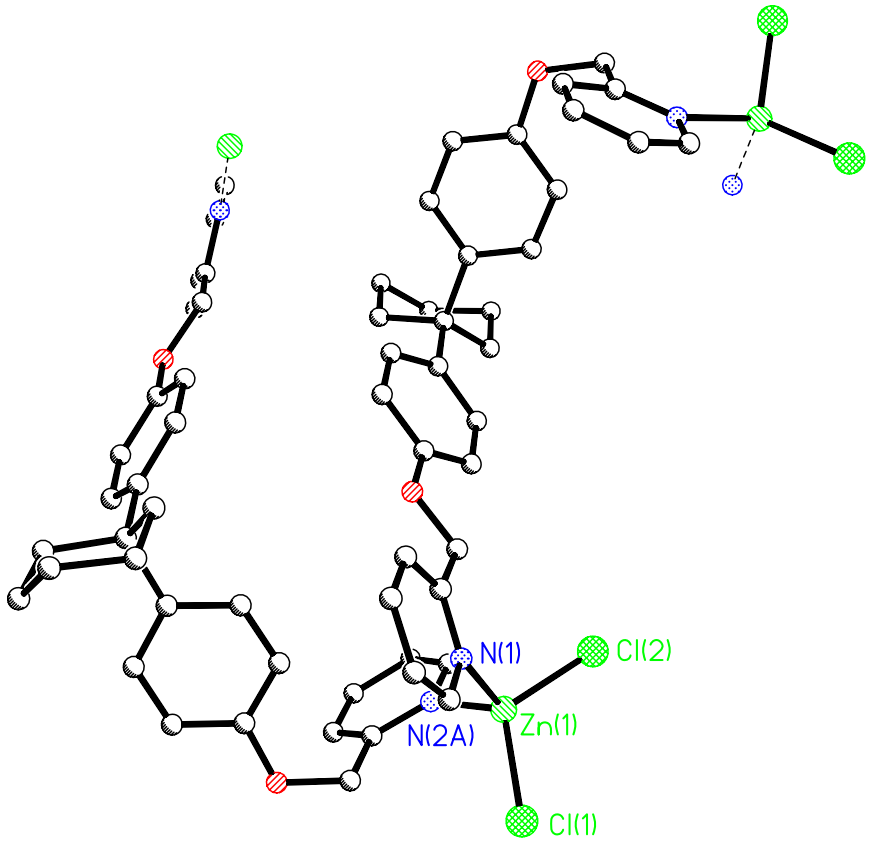


Figure 2.79 - *A small section of the one-dimensional helical polymer* ***2.74****. The complex is grown to show the overall connectivity of structure. Selected bond lengths (Å) and bond angles(°): Zn1-N1 2.098(2), Zn1-N2A 2.086(2), Zn1-Cl1 2.214(5), Zn1-Cl2 2.212(5), N2A-Zn1-N1 106.38(6), N1-Zn1-Cl1 105.82(5), N1-Zn1-Cl2 109.89(5), N2A-Zn1-Cl1 111.47(5), N2A-Zn1-Cl2 106.06(5), Cl2-Zn1-Cl1 116.81(2).*

The zinc atom has a distorted tetrahedral geometry coordinated to two pyridine nitrogen atoms of two separates ligands and two chlorine atoms. The largest deviation from tetrahedral arises between the chlorine atoms with an angle of 116.8°. The Zn-N bond lengths are 2.098Å and 2.086Å, which are normal. The Zn-Cl bond lengths of 2.212Å and 2.214Å are also similar to the previous zinc chloride complexes reported in this thesis.

The helical polymer propagates by a two-fold screw axis in an undulating fashion along the helical b-axis. Each ligand bridges two zinc atoms with the zinc atoms binding to two chlorine atoms and two pyridine nitrogens from separate ligands. Each ligand acts as an ‘L’ shaped bridge with the zinc atom connected to two such ligands that are related by a two-fold screw axis. The ‘L’ shaped ligands flip orientation between zinc

atoms, so that each zinc atom is coordinated to a pyridine ring above and a pyridine ring below. As a result the ligands alternate in orientation along the chain to give a helical polymer as shown in figure 2.80, with the hydrogens removed for clarity. The ligand crystallises in a centrosymmetric space and therefore must contain both left- (M) and right-handed (P) helices that are related by symmetry. The structure of the M-helix is depicted in figure 2.80. The pitch distance is 10.715Å, which is equal to the length of the b-axis, and is defined by the distance taken by two ligand molecules and two zinc atoms along the polymer chain. As expected, the pitch distance is slightly longer than the distance traversed between adjacent zinc atoms in the zinc bromide complex **2.73**.

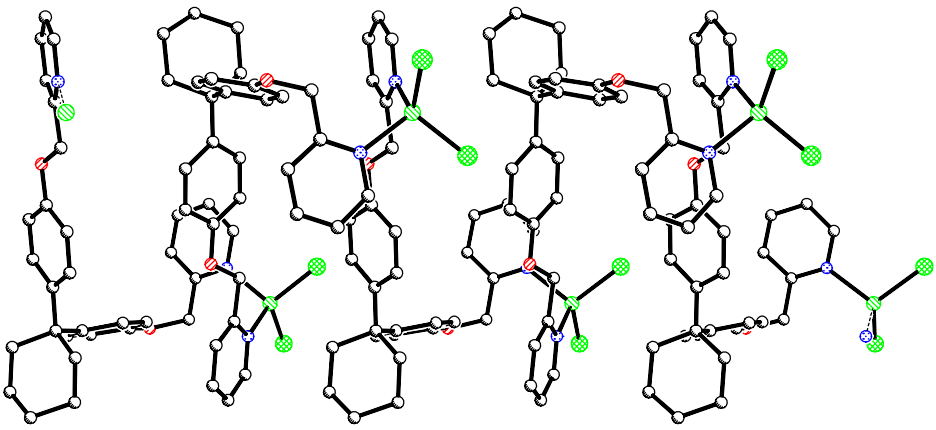


Figure 2.80 – *A section of the one-dimensional helical coordination polymer of* ***2.74****.*

This helical zinc coordination polymer is quite different to all the other one-dimensional helical coordination polymers described so far in this thesis. The other zinc one-dimensional helical coordination polymers described so far mainly have more elongated complex structures due to there being no severe twisting of the ligand molecules as they wrap and twist around the zinc atoms. In comparison, the ligand/zinc strands in complex **2.74** twist more severally with the ligand/zinc units almost overlapping on top of each other. In fact, complex **2.74** is quite similar to the helical zinc bromide complex **2.50** made with the 3-substituted methylpyridine Bisphenol A cored ligand, discussed in the previous section. In conclusion, the extension of ligand **2.69** to a two-atom spacer group has allowed the ligand to have more flexibility to generate two quite different helical complexes with quite different shapes.

*Other complexes with ligand **2.69***

Complexation of ligand **2.69** was attempted with only a few metal salts, due to only a small amount of ligand being isolated. Ligand **2.69** was reacted with $CuCl_2$, CuI, $Cu(NO_3)_2$, $ZnCl_2$, $ZnBr_2$, $PdCl_2$, $AgPF_6$, $AgCF_3SO_3$ and $AgClO_4$. A selection of these metal salts gave X-ray quality crystals with ligand **2.69**, which have already been discussed in detail. Unfortunately X-ray quality crystals or crystalline solids were not formed with all of these metals. Some of the complexes gave precipitates immediately, however despite several attempts these complexes could not be recrystallised and were not analysed any further.

Reaction of ligand **2.69** with $PdCl_2$ gave an orange precipitate immediately. The orange precipitate revealed a 1:1 complex, consistent with the formation of a discrete complex or coordination polymer. The polymer could be a one-dimensional helical coordination polymer, similar to that formed with the zinc metal salts.

Summary

This chapter described the synthesis and properties of a range of new two armed flexible bridging ligands derived from the commercially available precursors Bisphenol A and Bisphenol Z. The bisphenols were reacted with various haloazines and chloromethylpyridines to generate a range of new and novel symmetric flexible ligands. In total fourteen new flexible ligands were synthesised. Single crystal X-ray structures of some of the ligands were obtained to confirm their structures and determine their overall conformation in the solid state. Six crystal structures of ligands derived from Bisphenol A were solved and three structures of the Bisphenol Z derived ligands. The new ligands were successfully reacted with a variety of metal salts to generate a wide range of metallosupramolecular structures.

Overall the Bisphenol A cored ligands proved to be very successful as synthons for metallosupramolecular chemistry, generating a wide variety of structures. The 2-pyridine substituted ligand **2.19** was reacted with a range of metal salts to provide a selection of one-, two- and three-dimensional structures. A range of one-dimensional coordination polymers with different metal salts were fully characterised by X-ray

crystallography, including several helical one-dimensional polymers and an interesting necklace-like polymer chain composed of M_2L_2 macrocyclic units inter-linked by Cu_2Cl_4 squares that had the appearance of a belcher chain necklace. A couple of [2+2] macrocycles also formed with ligand **2.19** exhibiting rectangular topologies with the metal atoms making up the short sides of the rectangle in one structure and metal atoms as part of the long side of the rectangle in another. However, the most fascinating structure synthesised with ligand **2.19** is the copper(II) dinuclear quadruple helicate made with $Cu(NO_3)_2$. There have only been a few quadruple helicates described in the literature and to the best of our knowledge this is the first such example of a dinuclear quadruply-stranded helicate having square-pyramidal metal termini. Consequently, this structure belongs to a very rare group of complexes. The unpredictability of the structures was reflected in the diverse range of products obtained. Ligand **2.19** proved to be a very versatile synthon in metallosupramolecular chemistry by generating such a wide range of complex structures.

Unfortunately, no complexes suitable for X-ray analysis were crystallised with the Bisphenol A backboned ligands **2.23** and **2.25,** containing the larger heterocyclic ring systems quinoline and quinoxaline. This could be due to the inherent low solubility of these ligands and the bulkier π ring system. Only one complex was able to be fully characterised with the pyrazine substituted ligand **2.21**, which was a discrete [2+2] macrocycle, with the copper chloride coordinating to the less hindered nitrogen atom of the pyrazine.

Extension of the Bisphenol A derived ligands to two-atom spacer groups was also investigated with ligands **2.45**, **2.47** and **2.49**. These more flexible ligands were reacted with a variety of metal salts; however, the complexes did not seem to crystallise as readily as the complexes with other ligands and only a couple of complexes were fully characterised. X-ray analysis revealed one-dimensional polymeric structures with quite different topologies, both exhibiting *anti* and *gauche* conformations in the ligand binding arms. The addition of a two-atom spacer group appears to allow more flexibility in the ligand so it can wrap and twist around metal atoms more creatively to give interesting structures.

The Bisphenol Z based ligands also proved to be versatile synthons for the construction of metallosupramolecular species. The 2-substituted pyridine ligand **2.53** primarily

formed one-dimensional helical coordination polymers that were found to be isomorphous to one another but not quite isostructural. These helical polymers were very similar to the helical polymers made from the Bisphenol A derived 2-substituted pyridine ligand **2.19**. Also, a necklace-like polymer composed of M_2L_2 macrocyclic units linked by the unique copper motif with copper atoms with different coordination geometries was made from $CuCl_2$. Necklace-like polymers also formed with the pyrazine substituted ligand **2.54**, one of which has octahedral cobalt atoms that act as spiro centers linking together square macrocycles.

Complexes with the Bisphenol Z ligands **2.55** and **2.56** were unable to be crystallised. Once again this could be because of the inherent low solubility of these ligands and the much larger and bulkier π ring system.

Isomeric chloromethylpyridines were substituted onto the Bisphenol Z backbone to provide more flexibility to the ligand by creating a two-atom spacer group. These more flexible ligands were reacted with a variety of metal salts to generate a range of discrete and polymeric structures that were able to be fully characterised. Both discrete and polymeric complexes were constructed with the 2- and 3-substituted methylpyridine ligands **2.68** and **2.69**, with the 2-substituted ligand **2.69** being the most successful. Interestingly, all the complexes exhibited *anti* and *gauche* conformations in the binding arms of the ligand. The extra flexibility of the two-atom spacer group allows the formation of more intricate complexes with more severe twisting of the ligand around the metal atoms, due to the flexible chain tilting the aromatic rings. In general one might expect to observe all *anti* backbones in flexible ligands as these are more energetically stable in comparison to the *gauche* conformation.

Numerous weak interactions were observed in all the crystal structures of the ligands and complexes. Due to the conformation and orientation of the ligands in the solid state and in the complexes, predominantly edge-to-face π interactions were observed rather than π-π stacking interactions. Numerous hydrogen bonding interactions also occurred between ligand molecules, solvent molecules and counterions in the crystal lattices.

Chapter Three

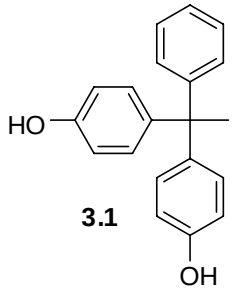
Bisphenol AP based ligands

Chapter Three

Bisphenol AP based ligands

Introduction

To further investigate the potential of two-armed bridging ligands as synthons in metallosupramolecular chemistry a new series of less symmetrical Bisphenol AP based ligands were synthesised. This series of ligands was based around a Bisphenol AP core, which is essentially an extension of Bisphenol A by addition of another phenyl group. The structure of Bisphenol AP, commercially known as 4,4'-(1-phenylethylidene)bisphenol, is shown in figure 3.1. The ligand precursor **3.1** consists of a central quaternary carbon atom core with a methyl group substituent in the terminal ancillary position. Three benzene rings are tethered to the remaining sites around the quaternary carbon, two of which are terminated by alcohol functional groups that will be further substituted with heterocyclic donor groups to generate a new range of two-armed bridging ligands. If the third remaining benzene ring also had an alcohol functional group a tripodal structure would be created. Tripodal ligands of this nature have also been synthesised and will be discussed in chapter four.



3.1

Figure 3.1 – *Structure of Bisphenol AP.*

The benzene ring is effectively just a bulkier substituent group that generates a less symmetrical ligand. Symmetry in bridging ligands is a very important aspect of ligand design, because symmetrical ligands are more likely to encourage the self-assembly of a singular crystalline product. In contrast, studies have shown that less symmetrical ligands are less likely to give a single supramolecular architecture. Therefore it is of

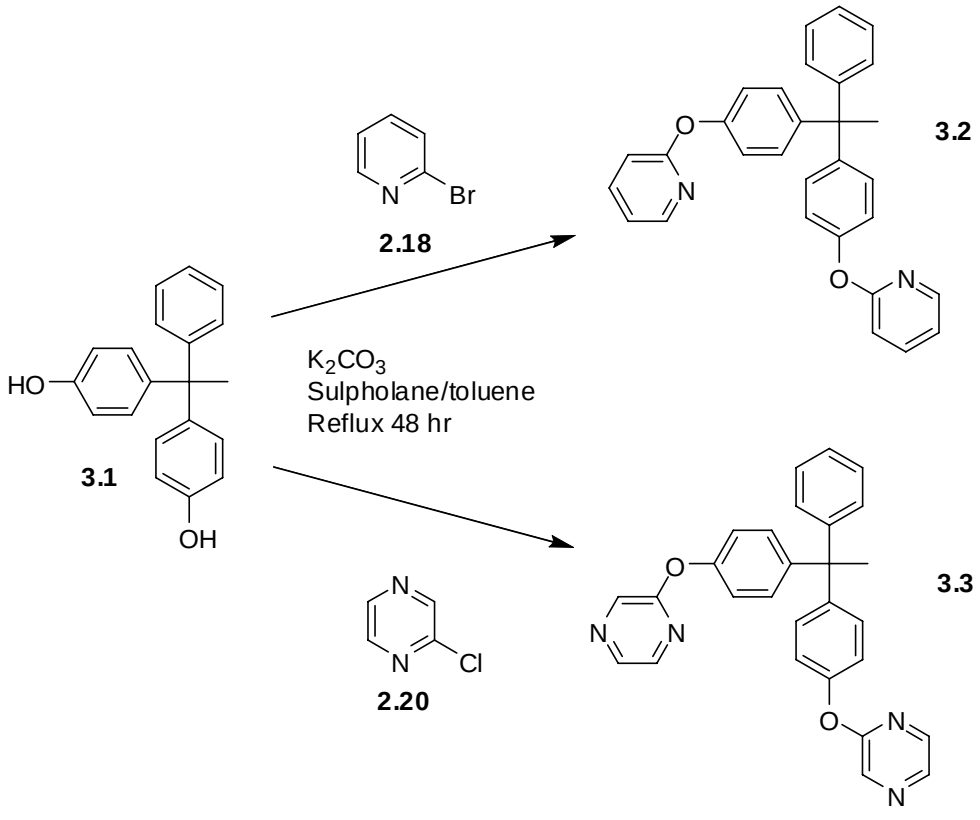
great interest to further investigate less symmetrical ligands by creating a family of ligands based around the Bisphenol AP core and investigating their ability as synthons in metallosupramolecular chemistry.

Another reason to explore the metallosupramolecular chemistry of the Bisphenol AP derived ligands is the potential silver-arene interactions between the auxiliary benzene ring and silver(I) atoms. The terminal benzene ring could potentially participate in such silver-benzene interactions, which are highly topical at the moment. Silver-benzene interactions are where the silver atom is positioned above the aromatic ring close enough to interact with one or more of the carbon atoms in the aromatic ring. It has been found that in general the silver atom is more likely to coordinate in an unsymmetrical fashion to one or two carbon atoms in the aromatic ring as opposed to lying above the centre of the benzene ring and interacting with all the carbon atoms in a η^6 fashion.[193-196] Such η^1 and η^2 silver-arene interactions are quite common in metallosupramolecular chemistry and there have been many examples reported in the literature, although the η^1 silver-arene interactions are not as common as η^2. Typical silver-carbon interaction distances in complexes between the closest carbon atom of the arene ring range between 2.45-2.49Å and the next closest silver-carbon interaction ranges between 2.6-2.9Å.[193] Obviously the longer the silver-carbon distance the weaker the coordination and interaction. Metal-arene interactions are not just limited to silver ions and other transition metal ions can potentially have strong interactions with arene rings. Some examples of other metal ions that are known to participate in such interactions are copper,[197, 198] ruthenium,[199] palladium and platinum, to name just a few.

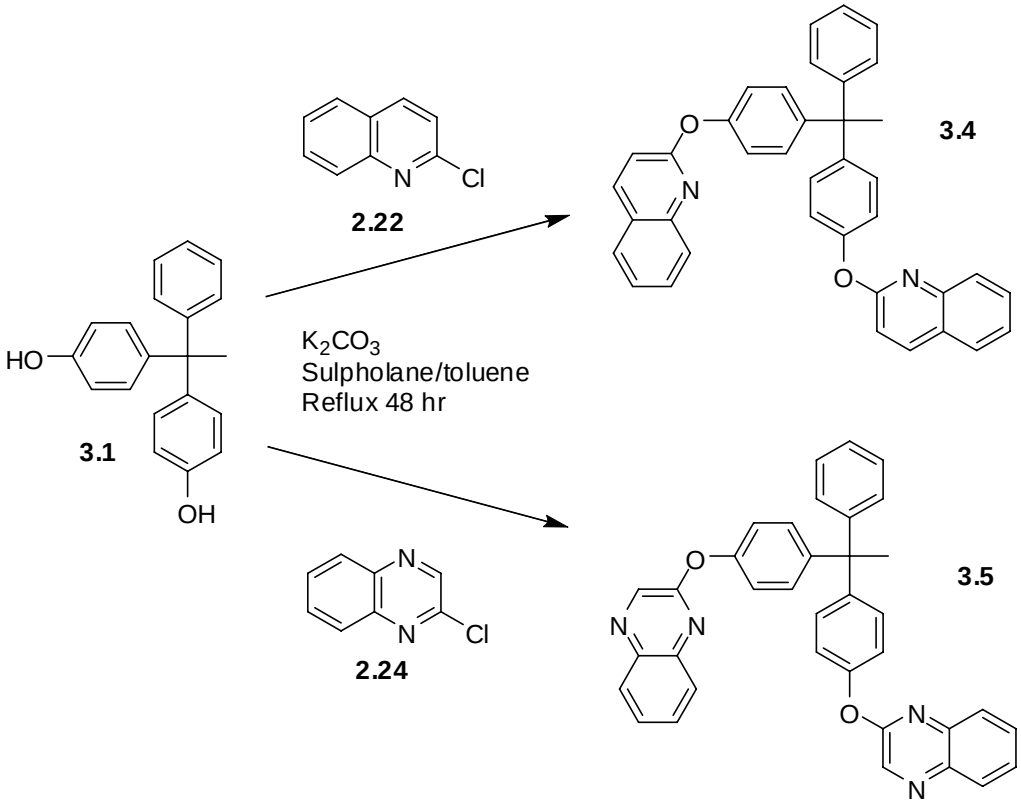
This chapter investigates a new range of flexible bridging ligands derived from the Bisphenol AP core. It will be interesting to investigate these less symmetrical Bisphenol AP ligands to see if less internal symmetry will potentially enhance or hinder the formation of complexes. In particular it will be interesting to observe any cation-π interactions between the aromatic rings and various metal ions.

Synthesis of the Bisphenol AP based -O- spaced ligands

All four one-atom oxygen spaced ligands synthesised from ligand precursor **3.1** are outlined in Scheme 3.1 and Scheme 3.2. The new ligands **3.2**, **3.3**, **3.4** and **3.5** containing diaryl ether linkages were synthesised by double nucleophilic aromatic substitution of Bisphenol AP (**3.1**) with the haloazines **2.18**, **2.20**, **2.22** and **2.24**. This synthetic route is identical to the synthesis of the oxygen spaced Bisphenol A and Bisphenol Z bridging ligands described in chapter two and is analogous to that of O'Keefe et al.[112] All four of these crude ligands were recrystallised from an acetone/water solution to give white or yellow crystalline solids in reasonable yields. The white crystalline solids of ligands **3.2** and **3.3** were obtained in good yields of 84% and 97%, respectively. The yellow crystalline solids of ligands **3.4** and **3.5** were also obtained in good yields of 69% and 60%, respectively. All four ligands were subsequently fully characterised by elemental analyses, mass spectrometry, melting points and ^{1}H NMR and ^{13}C NMR spectroscopy.[113]



Scheme 3.1 – *Synthesis of ligands **3.2** and **3.3**.*



Scheme 3.2 – *Synthesis of ligands **3.4** and **3.5**.*

Single crystal X-ray structures of ligands **3.2**, **3.3** and **3.5** were also obtained to confirm their structures and overall conformations in the solid state. In this project it was important to obtain the structures of the ligands as well as the complexes in order to fully understand and investigate the conformational flexibility of the ligand in the solid state in both cases.

Crystal structure of ligand 1,1-di(4-(2-pyridyloxy)phenyl)phenylethane, 3.2

Large colourless crystals of ligand **3.2** suitable for X-ray crystallography were furnished from slow evaporation of an acetone solution of the ligand. Ligand **3.2** crystallises in the monoclinic space group $P2_1/c$ with a full ligand molecule in the asymmetric unit, as shown in figure 3.2. In ligand **3.2** the three central benzene rings twist around the central quaternary carbon in a propeller-like fashion. This can be more clearly seen if one looks down through the methyl group of the ligand on a space-filling diagram as shown in figure 3.3. Any potential mirror symmetry is lost in ligand **3.2**, as a consequence of the twisting of the benzene rings about the quaternary carbon atom and

the different conformations adopted by the pyridyl ether groups. The two pyridine rings are almost perpendicular to the attached benzene rings, both pointing inwards towards the centre of the benzene rings. The nitrogen donor atoms are also pointing inwards towards the central cavity between the two benzene rings, with a separation of 8.388Å.

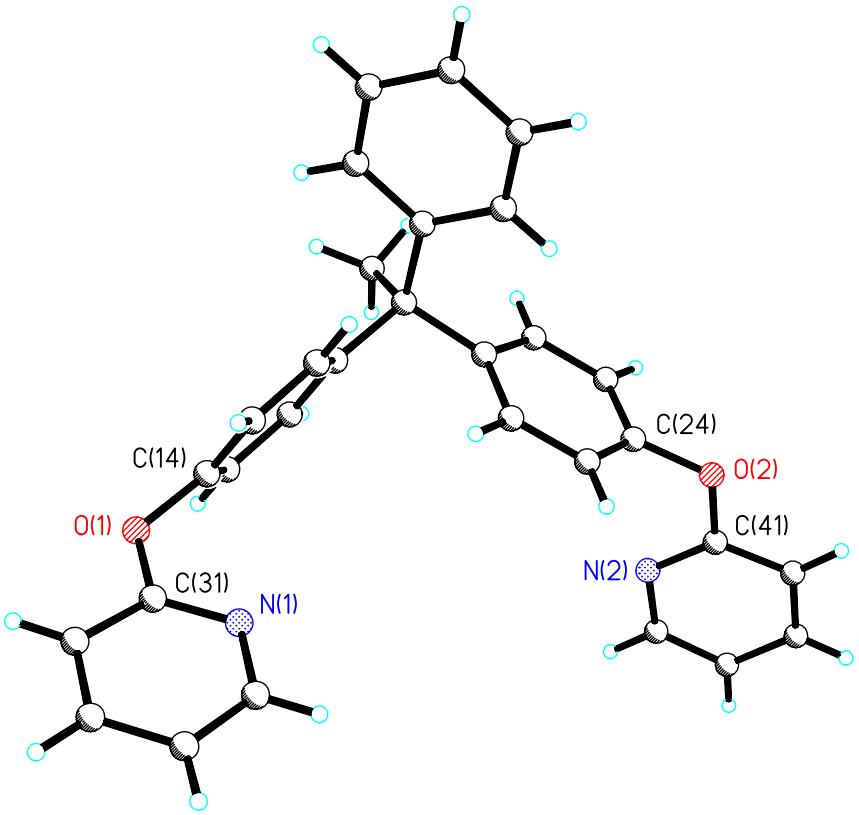


Figure 3.2 – *X-ray crystal structure of ligand* ***3.2****. Selected bond lengths (Å) and bond angles (°): C14-O1 1.409(2), O1-C31 1.383(2), C31-N1 1.316(2), C24-O2 1.412(2), O2-C41 1.378(2), C41-N2 1.320(2), C31-O1-C14 117.9(1), N1-C31-O1 118.6(2), C41-O2-C24 118.4(1), N2-C41-O2 118.9(1).*

In the packing diagram of ligand **3.2** there are only a few significant interactions between ligand molecules and no observed π-π stacking or edge-to-face interactions. One of the few interactions observed involves the nitrogen atoms of the ligands hydrogen bonding to the benzene ring hydrogen atoms of adjacent ligand molecules.

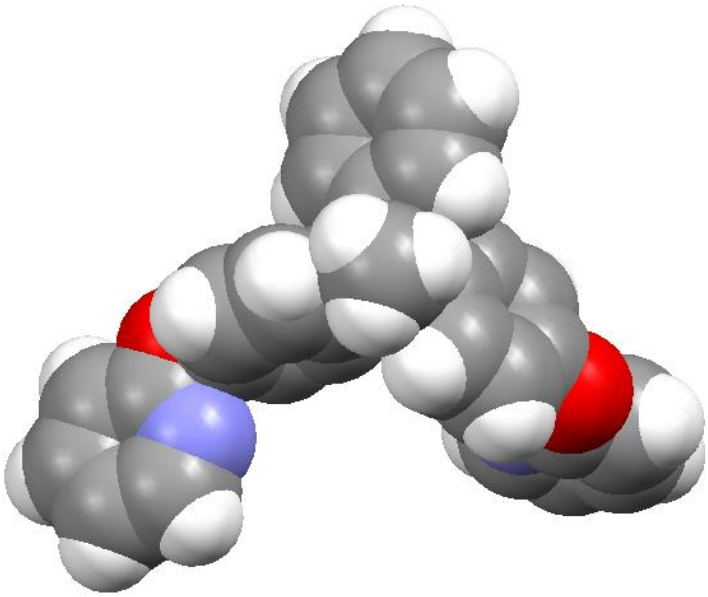


Figure 3.3 – *Space-filling diagram of ligand **3.2**. View when looking down through the methyl group illustrating the propeller-like twisting around the three central benzene rings.*

Crystal structure of ligand 1,1-di(4-(2-pyrazinyloxy)phenyl)phenylethane, 3.3

Crystals of ligand **3.3** were grown from a solution of the ligand with zinc bromide. The structure of ligand **3.3** crystallises in the orthorhombic space group $Pna2_1$ with a full molecule in the asymmetric unit, as depicted in figure 3.4. Once again the three central benzene rings of the ligand twist around the quaternary carbon in a propeller-like way, similar to ligand **3.2**. In fact, ligand **3.3** adopts such a similar conformation in the solid state to ligand **3.2** that the ligands are almost identical to one another. The only difference between the ligands is the different heterocycles appended. In compound **3.3** the pyrazine rings are facing perpendicular to the mean planes of the attached benzene rings, with the internal nitrogen atoms twisted to point inwards towards the central cavity between the two benzene rings. The external nitrogens are orientated to face outwards and are therefore more likely to coordinate to metal atoms, because of the less sterically hindered position of the nitrogen atoms on the ligand. The distance between the internal nitrogen atoms is 8.488Å, whereas the distance between external nitrogen atoms is longer at 12.861Å. Overall the ligand has a very similar compact structure to ligand **3.2**, with the overall shape of the ligand reflected in the low N-C-O-C torsional angles of 6.64° and 19.56°.

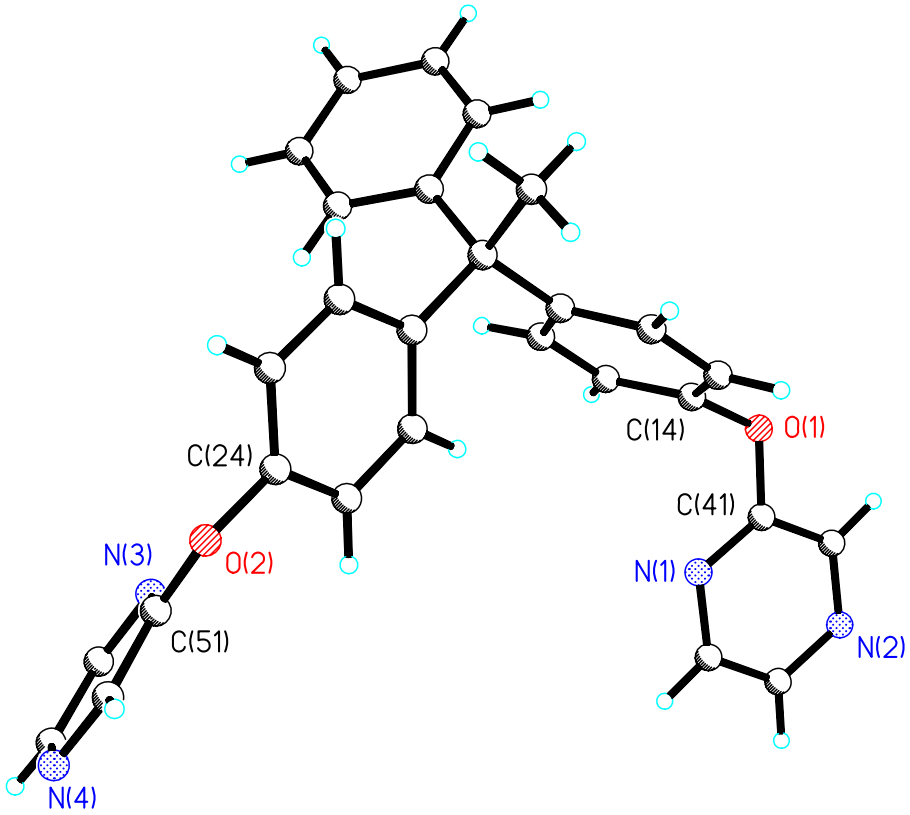


Figure 3.4 – *X-ray crystal structure of ligand* ***3.3****. Selected bond lengths (Å) and bond angles (°): C14-O1 1.410(3), O1-C41 1.358(3), N1-C41 1.315(3), C24-O2 1.403(3), O2-C51 1.365(3), N3-C51 1.312(3), C41-O1-C14 118.8(2), N1-C41-O1 120.4(2), C51-O2-C24 120.7(2), N3-C51-O2 120.3(2).*

In the packing the ligands stack on top of each other into a chain of ligands that link through edge-to-face interactions between the pyrazine rings and the benzene rings of one of the binding arms (2.543Å). These chains of ligands are further linked to other ligand chains through hydrogen bonding interactions between the pyrazine nitrogens and pyrazine hydrogen atoms to generate sheets of ligand chains. No π-π stacking interactions were observed.

Crystal structure of ligand 1,1-di(4-(2-quinoxalinyloxy)phenyl)phenylethane, 3.5

Yellow crystals of ligand **3.5** were obtained from a mixed solution of the ligand and zinc chloride in methanol. Once again the structure of ligand **3.5** is quite similar to that of the previous two Bisphenol AP derived ligands **3.2** and **3.3**. Ligand **3.5** crystallises in the monoclinic space group $P2_1/n$ with the full ligand molecule in the asymmetric unit, as shown in figure 3.5, and no solvent molecules or zinc chloride. Any potential mirror symmetry is lost in ligand **3.5** in the solid state, due to the propeller-like twisting of the three benzene rings about the central quaternary carbon and the different conformations of the two quinoxaline ether groups. The quinoxaline heterocyclic rings are perpendicular to the attached benzene rings with both the internal nitrogen donor atoms pointing inwards towards the centre of the attached benzene rings. As a consequence, the quinoxaline rings are also pointing in opposite directions to one another. The propeller-like twisting of the benzene rings around the quaternary carbon and the quinoxaline group's relative orientation to the attached benzene rings, are better accentuated in the space-filling diagram depicted in figure 3.6. The distance between the internal nitrogen donor atoms is 9.137Å, whereas the distance between the external nitrogen donor atoms is 13.768Å. The less hindered external nitrogen atoms face outwards and are consequently more likely to coordinate to metal atoms. The overall conformation of the ligand is reflected in the very low N-C-O-C torsional angles of 0.01° and 5.37°.

In the packing diagram, adjacent ligand molecules stack into chains via π-π stacking interactions between quinoxaline rings (3.290Å). The chains of ligands are further inter-linked to other ligand chains through edge-to-face interactions between the benzene rings of the ligands binding arms (2.799Å) to generate a sheet of ligands. Sheets of ligands are further linked via edge-to-face interactions, with the edge of one benzene ring orientated towards the face of an adjacent benzene ring (2.699Å).

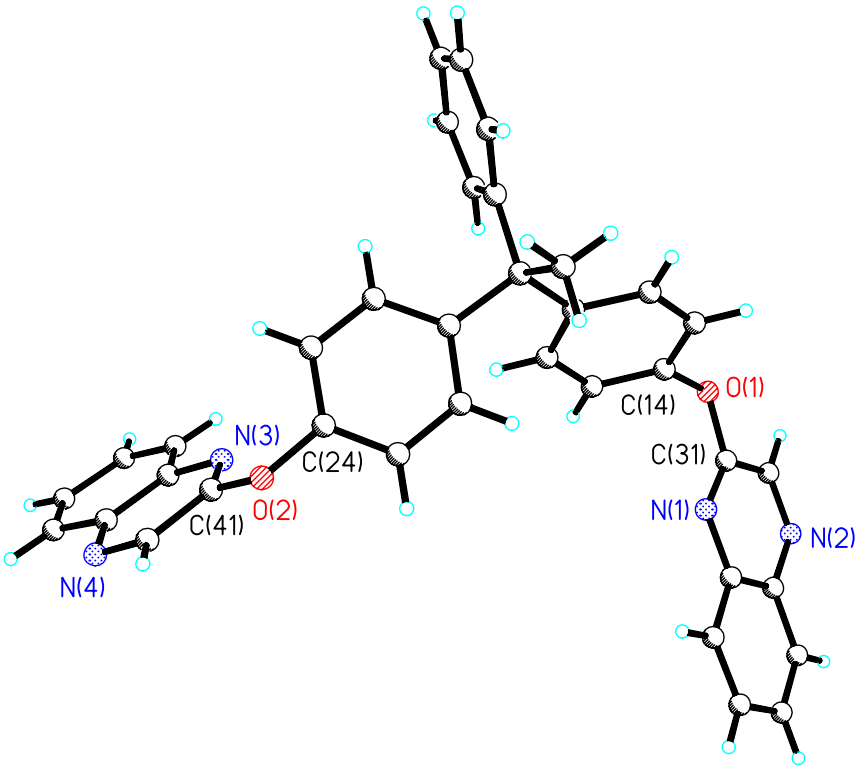


Figure 3.5 – *X-ray crystal structure of ligand* ***3.5****. Selected bond lengths (Å) and bond angles (°): C14-O1 1.406(2), O1-C31 1.360(2), C31-N1 1.288(2), C24-O2 1.401(2), O2-C41 1.361(2), C41-N3 1.290(2), C31-O1-C14 120.1(1), N1-C31-O1 122.0(2), C41-O2-C24 119.5(1), N3-C41-O2 122.2(2).*

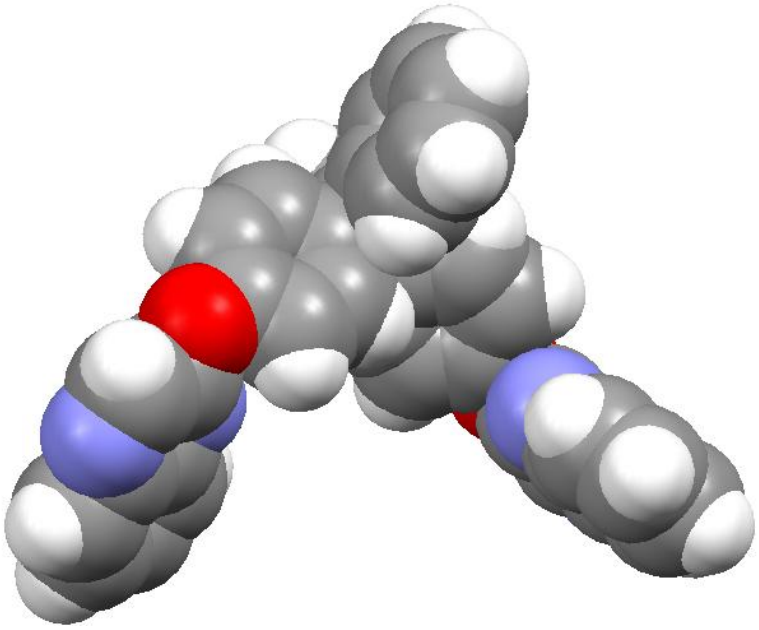


Figure 3.6 - Space-filling diagram of ligand **3.5**.

A literature search revealed only two closely related compounds to the Bisphenol AP derived ligands, which are shown in figure 3.7. Both of the ligands, shown in figure 3.7, have a very similar Bisphenol AP backbone to the ligands synthesised above and have also been used as synthons to construct metallosupramolecular species. Ligand **3.6** is very similar to the Bisphenol AP derived ligands having an identical backbone with a central quaternary carbon atom tethered to three benzene rings as well as a terminal methyl group. Two of the ligand arms are further coordinated to alkyne groups as opposed to nitrogen heterocyclic groups. McArdle and co-workers have made a series of similar ligands by simply varying the hinge groups on the ligand backbone, some of which were discussed in chapter two.[117] In order to make complexes, McArdle and co-workers first converted ligand **3.6** to a dialkynyldigold(I) ligand precursor and then reacted it with diphosphine ligands to produce a macrocycle. Ligand **3.7** is also very similar to the Bisphenol AP ligands mentioned above by having the same Bisphenol AP backbone with diphosphine groups attached instead of nitrogen heterocycles. Van der Vlugt et al. have described a series of such diphosphine ligands based around bisphenol-type backbones.[178, 179] Unfortunately, no X-ray structures of complexes have been characterised so far.

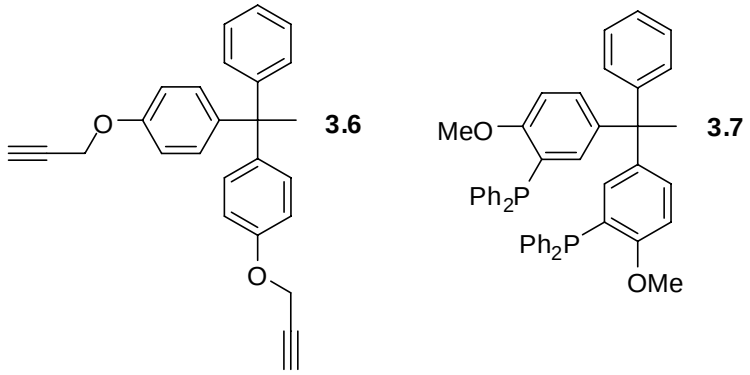


Figure 3.7 – *Structurally similar ligands to the Bisphenol AP derived ligands.*

Complexes with ligand 3.2

*Crystal structure of the complex with $AgPF_6$ (**3.8**)*

Ligand **3.2** was dissolved in chloroform and layered upon silver hexafluorophosphate dissolved in acetone. Ethyl acetate was slowly diffused into the reaction mixture and slow evaporation over time produced colourless plate-like crystals that were suitable for X-ray crystallography. The complex crystallises in the monoclinic space group C2/c generating a dimeric M_2L_2 macrocycle, which is shown in figure 3.8. The hydrogens, disordered hexafluorophosphate anion and disordered chloroform solvent molecule have been excluded for clarity.

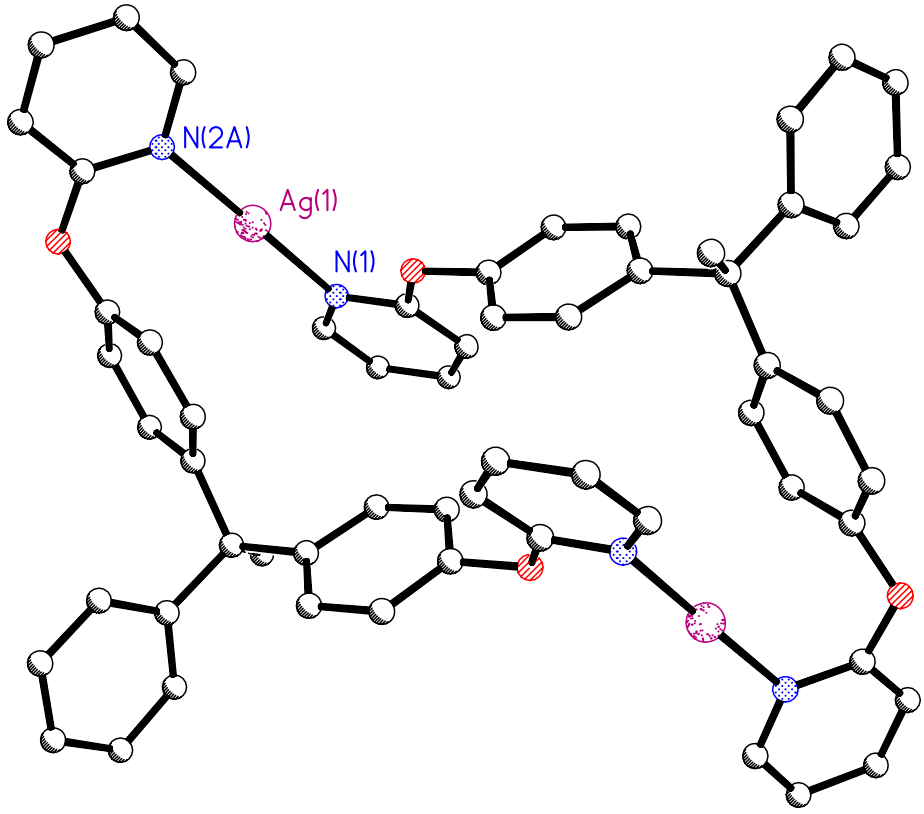


Figure 3.8 – *View of the dimeric M_2L_2 macrocycle **3.8**. Selected bond lengths (Å) and bond angles (°): Ag1-N1 2.154(5), Ag1-N2A 2.163(5), N1-Ag1-N2A 179.2(2).*

The asymmetric unit of **3.8** contains one whole ligand, a silver atom, one disordered hexafluorophosphate anion and a disordered chloroform solvent molecule. The M_2L_2 macrocycle is formed about a centre of inversion at the centre of the macrocycle. Each silver atom is coordinated to two pyridine rings with a linear coordination geometry of

179.2°. The silver-pyridine bond lengths of 2.163Å and 2.154Å are similar to other related two-coordinate silver(I) complexes in this thesis. In complex **3.8**, the ligand adopts a similar conformation to that of ligand **3.2** in the solid state with the three central benzene rings twisted around the quaternary carbon atom in a propeller-like fashion. The difference between the conformation of the ligand **3.2** in the solid state and ligand **3.2** in complex **3.8** is the different conformations adopted by the pyridyl ether groups of the ligand. In the silver complex **3.8** the two pyridine rings are tilted to orient themselves perpendicular to the attached benzene rings, with one of the nitrogen atoms pointing inwards towards the central cavity between the two benzene rings and the other pointing outwards away from the central cavity. This is in contrast to ligand **3.2** in the solid state in which both nitrogen donor atoms are pointing inwards towards the central cavity between the two benzene rings.

As a consequence of the propeller-like twisting of the ligand backbone the dimeric M_2L_2 macrocycle does not seem to adopt any particular square or rectangular shaped macrocycle. This is in contrast to other previously mentioned [2+2] macrocycles that often adopted rectangular-like topologies with the metal atoms forming either the short sides of the rectangle or part of the long sides of the rectangle. In complex **3.8** the silver atoms are diagonal to one another at a distance of 10.220Å. There are no observed intramolecular π-π stacking interactions between the aromatic rings within a macrocyclic unit, due to the conformation and orientation of the aromatic rings in the macrocycle. The absence of such π-π interactions is unusual, because such interactions are known to stabilise macrocycles, however they are not a necessity for the formation of such [2+2] macrocycles.[164] There are no observed π-π interactions between aromatic rings, because two of the binding arms benzene rings are almost coplanar to one another as well as significantly offset from one another. In fact, as a consequence of the conformation of the ligand, all the aromatic rings are significantly displaced from one another making it harder for intramolecular π-π interactions to occur.

There is no void in the centre of the macrocycle as a result of the unusually shaped ligand and the way in which it entwines around the silver atom. The absence of any internal cavity is illustrated in a space-filling diagram of the macrocycle **3.8** shown in figure 3.9.

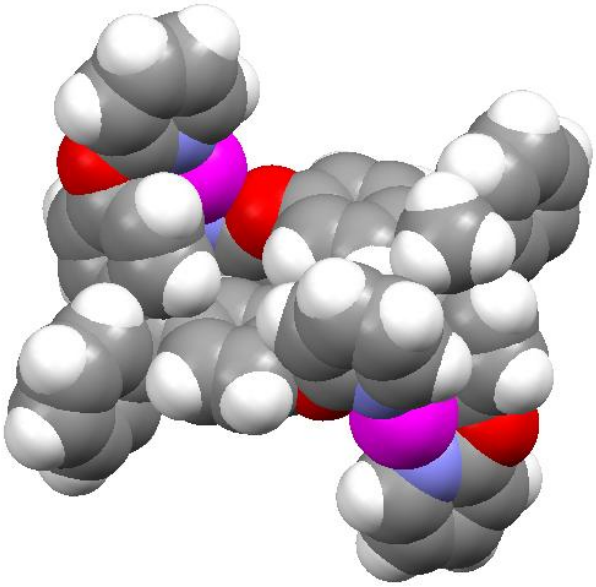


Figure 3.9 – *Space-filling diagram of the M_2L_2 macrocycle **3.8**.*

In the extended structure the macrocycles pack into chains of dimers via edge-to-face interactions between the auxiliary benzene rings and the bridging benzene rings of adjacent macrocycles (2.734Å). The solvent molecules and the hexafluorophosphate anions fill in voids around the chains. Unfortunately, even in the extended structure the auxiliary benzene ring does not participate in any η^1 or η^2 interactions between aromatic rings and the silver(I) atoms.

*Other complexes with ligand **3.2***

The Bisphenol AP derived ligand **3.2** was reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(ClO_4)_2$, $Cu(NO_3)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $ZnCl_2$ and $ZnBr_2$. Crystals suitable for X-ray analysis studies were obtained of a dimeric silver M_2L_2 macrocyclic complex, which was discussed in detail above. Regrettably, no crystals of other complexes suitable for X-ray analysis were obtained. Most of the complexes formed with ligand **3.2** gave solids upon slow evaporation of the reaction mixture. Some of the solids were further characterised and analysed by elemental analysis.

Complexation of ligand **3.2** with $CoCl_2$ gave a blue crystalline solid upon slow evaporation that analysed as a M_2L complex. Slow evaporation of the reaction mixture containing ligand **3.2** and $Cu(ClO_4)_2$ produced a blue solid on standing that analysed as a M_2L_3 compound. This stoichiometry suggests the formation of a complicated coordination polymer or potentially something even more interesting like a triple helicate or a M_4L_6 tetrahedral cage. Unfortunately attempts to recrystallise this complex were unsuccessful.

Two other silver complexes were also made with ligand **3.2** under the same conditions as complex **3.8**. Reaction of ligand **3.2** with $AgClO_4$ produced a white crystalline solid that analysed with a 1:1 ratio. Slow evaporation of a reaction mixture containing ligand **3.2** and $AgCF_3SO_3$ gave a crystalline solid that analysed as a M_3L_2 compound with no solvent. This stoichiometry is unusual and suggests the formation of a complicated coordination polymer.

Complexes with ligand 3.3

The pyrazine substituted Bisphenol AP derived ligand **3.3** was reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(ClO_4)_2$, $Cu(NO_3)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $ZnCl_2$ and $ZnBr_2$ under different conditions. Unfortunately, no crystals of any of the complexes were able to be grown. Insoluble precipitates formed almost immediately upon mixing of the solutions, which were subsequently unable to be recrystallised with most common solvents, even DMSO. Sometimes instead of complexation, crystals of either the ligand and/or metal salt were grown straight from the complex solution. This was how the structure of ligand **3.3** was elucidated.

Reaction of ligand **3.3** with CuI gave a pale orange crystalline precipitate that analysed with a 1:1 ratio. Subsequently, complexes with 1:1 ratios were also obtained with the silver salts $AgPF_6$, $AgClO_4$ and $AgCF_3SO_3$. It is quite likely that all three of these silver compounds have similar structures.

Complexes with ligand 3.4

Complexation of ligand **3.4** was attempted with many different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(ClO_4)_2$, $Cu(NO_3)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $Pd(PhCN)_2Cl_2$, $ZnCl_2$ and $ZnBr_2$. Regrettably, no crystals suitable for X-ray analysis were obtained with either the ligand itself or any complexes. Most of the complexes that formed with ligand **3.4** were precipitates that formed immediately upon mixing. Attempts were made to recrystallise the precipitates with no success. A couple of the precipitates were further characterised and analysed by elemental analysis.

A white precipitate formed immediately on reaction of ligand **3.4** with $AgClO_4$ that analysed with a 1:1 ratio. This 1:1 ratio corresponds to the formation of either a discrete compound or more likely a coordination polymer.

Reaction of ligand **3.4** with $Pd(PhCN)_2Cl_2$ gave a brown crystalline precipitate immediately that analysed as an unusual M_3L_2 compound. Since ligand **3.4** can only bind to a maximum of two metals per ligand and there are three metals according to the stoichiometry, it seems likely that the structure has some sort of complicated palladium chloride metal motif included in the structure.

Complexes with ligand 3.5

Complexation of ligand **3.5** was attempted with only a few metal salts due to the small quantity of ligand available. Complexation of ligand **3.5** with most metal salts gave precipitates immediately that were insoluble and unable to be recrystallised. As a consequence no crystals of any complexes suitable for X-ray crystallography were obtained. A couple of the precipitates were further characterised and analysed by elemental analysis. Sometimes instead of complexation, crystals of either the ligand and/or the metal salt were grown from the mixed solution. This was how the structure of ligand **3.5** was elucidated from a mixed solution of ligand **3.5** with $ZnCl_2$.

A white precipitate formed immediately on reaction of ligand **3.5** with $AgClO_4$. The compound analysed as a M_3L_2 compound. Since ligand **3.5** has four nitrogen donor atoms it can coordinate up to a maximum of four metal atoms. Therefore, the M_3L_2 stoichiometry is right for the formation of a caged structure if the ligand coordinates

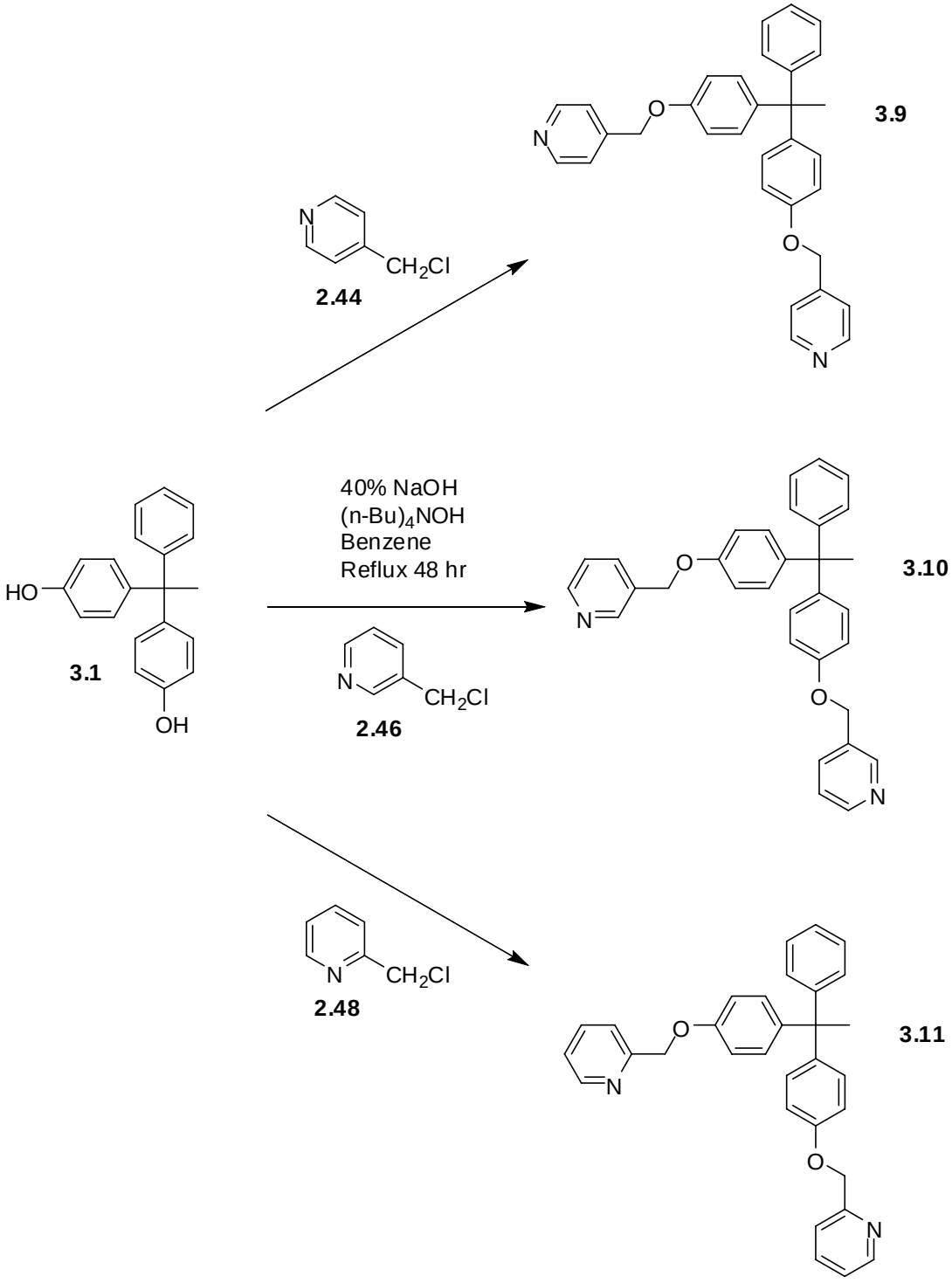
through three of the nitrogen donor atoms. Attempts were made to recrystallise the compound, unfortunately the precipitate was very insoluble which suggests the formation of a polymer species.

Reaction of ligand **3.5** with $Pd(PhCN)_2Cl_2$ gave a bronze coloured precipitate that formed immediately. The precipitate analysed as a M_2L compound.

Synthesis of the Bisphenol AP based -CH_2O- spaced ligands

Finally, three more Bisphenol AP derived ligands were synthesised with a two-atom spacer group instead of just one to complete the set of Bisphenol AP derived bridging ligands. The two-atom spacer group is a methyleneoxy group (CH_2O) which is positioned between the benzene ring and the 2-, 3- or 4-substituted pyridine ring. The extension of various ligands with such two-atom spacer groups has been greatly explored by previous members of the Steel group and the additional flexibility can often lead to more interesting and intricate assemblies.

The three two-atom methyleneoxy spaced ligands synthesised from ligand precursor **3.1** are outlined in Scheme 3.3. All three methyleneoxy spacer group ligands were synthesised via a phase-transfer-catalysed (PTC) alkylation reaction analogous to that of Hartshorn et al.[102, 172] This synthetic route is identical to the synthesis of the methyleneoxy spaced Bisphenol A and Bisphenol Z bridging ligands synthesised in chapter two. The double alkylation of Bisphenol AP with the three isomeric chloromethylpyridines gave crude ligands **3.9**, **3.10** and **3.11** which were subsequently recrystallised to give brown solids or a brown oil. Brown solids were isolated for ligands **3.9** and **3.10** in yields of 48% and 82%, respectively, whereas ligand **3.11** was isolated as an oil in 98% yield. All ligands were subsequently fully characterised by elemental analyses, mass spectrometry, melting points and ^{1}H NMR and ^{13}C NMR spectroscopy.[113]



Scheme 3.3 *– Synthetic route to the methyleneoxy spacer group ligands* ***3.9****,* ***3.10*** *and* ***3.11****.*

Unfortunately, despite numerous attempts, no crystals suitable for X-ray crystallography of either the ligands or their complexes were obtained. Many

complexes with the three ligands were prepared which are discussed in more detail below.

Complexes with ligand 3.9

The Bisphenol AP derived ligand **3.9** was reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(ClO_4)_2$, $Cu(NO_3)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $ZnCl_2$ and $ZnBr_2$ under a variety of conditions. Complexation of ligand **3.9** with all the metal salts gave precipitates immediately that were generally insoluble in most solvents and were therefore unable to be recrystallised. As a consequence, no crystal structures of any complexes suitable for X-ray crystallography were obtained. However, some of the compounds were further characterised and analysed by elemental analysis.

Reaction of ligand **3.9** with $CuCl_2$, $Cu(ClO_4)_2$ and $AgClO_4$ gave precipitates immediately that analysed with 1:1 ratios. Reaction of ligand **3.9** with $CoCl_2$ and CuI gave blue and/or yellow precipitates immediately that analysed as M_2L compounds.

Complexes with ligand 3.10

Complexation of ligand **3.10** was attempted with many different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(ClO_4)_2$, $Cu(NO_3)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $Pd(PhCN)_2Cl_2$, $ZnCl_2$ and $ZnBr_2$. All of the complexes that formed with ligand **3.10** were precipitates that formed immediately upon mixing. Attempts were made to recrystallise the precipitates with no success. A couple of the precipitates were further characterised and analysed by elemental analysis.

A yellow precipitate formed immediately on reaction of ligand **3.10** with $PdCl_2$ that analysed with a 1:1 ratio. An orange precipitate formed immediately with $Pd(PhCN)_2Cl_2$ that analysed as an unusual M_4L_3 compound with no solvents associated with it. Unfortunately, attempts to recrystallise this complex were unsuccessful.

Complexes with ligand 3.11

Ligand **3.11** was reacted with numerous metal salts under a wide variety of conditions. Regrettably no crystals of any of the complexes were suitable for X-ray analysis. Most of the complexes that formed with ligand **3.11** gave crystalline solids upon slow evaporation of the reaction mixture or precipitated immediately. A few of the compounds were further characterised and analysed by elemental analysis.

Reaction of ligand **3.11** with $PdCl_2$, $Pd(PhCN)_2Cl_2$, $AgClO_4$ and $AgPF_6$ gave precipitates immediately in the case of the palladium salts and crystalline solids with the silver salts that analysed with 1:1 ratios.

Slow evaporation of a solution containing ligand **3.11** and CuI produced a yellow solid that analysed as a M_2L compound. Noteworthy is the fact that all of the compounds analysed have similar melting points and four of them have the same stoichiometry. Therefore it is possible that they all have very similar structures.

Summary

This chapter described a series of seven new ligands based around the Bisphenol AP core. The new two-armed bridging ligands contained a central quaternary carbon core with three benzene rings and a methyl substituent attached. Two of the benzene rings were further linked to nitrogen heterocyclic groups with one or two-atom spacer groups between the two aromatic groups. The third auxiliary benzene ring is not attached to anything else and is effectively a bulky substituent. As a result of the terminal benzene group the Bisphenol AP derived ligands are unsymmetrical. Studies have shown that less symmetrical ligands are less likely to give single crystalline products. With this in mind experiments were carried out investigating the unsymmetrical Bisphenol AP derived ligands to see if less internal symmetry would potentially enhance or hinder the formation of complexes with these ligands.

In this chapter seven new Bisphenol AP derived ligands were synthesised and the X-ray structures of three of these were determined. The ligands were subsequently reacted with metal salts to prepare complexes. Although numerous complexes were made with all the ligands and a variety of metal salts only one X-ray crystal structure of a complex

was obtained. The complex identified by X-ray crystallography was with the ligand **3.2**, the result being a dimeric silver M_2L_2 macrocycle.

It was anticipated that the terminal benzene ring on the Bisphenol AP derived ligands may participate in cation-π interactions with some of the various metal ions, because such interactions are highly topical at the moment, especially between silver(I) atoms and aromatic rings. Unfortunately, only one silver complex was fully characterised by X-ray crystallography and it did not appear to participate in such interactions.

This chapter did prove that although complexes with the Bisphenol AP derived bridging ligands were easy to synthesis they were a lot harder to crystallise as a result of the less symmetrical structure of the ligands. This study supports the theory that less symmetrical ligands are less likely to give single crystalline products compared to more symmetrical ligands.

Chapter Four

Tripodal and other multi-armed ligands

Chapter Four

Tripodal and other multi-armed ligands

Introduction

One of the most appealing features of metallosupramolecular chemistry is the potential ability to design and construct supramolecular frameworks with specific topologies. With this idea in mind there has been a lot of interest in the construction of cage-like species with internal cavities. To date many reports have focused on the self-assembly of cage-like complexes with multidentate ligands and metal ions, because these complexes can potentially contain large enough cavities to encapsulate guest molecules and/or act as catalysts. Since multidentate ligands can potentially coordinate to multiple metal atoms they can act as more complex synthons and lead to the construction of more elaborate metallosupramolecualar assemblies.

Two-armed bridging ligands can only bridge two metal atoms often resulting in the construction of one-dimensional and two-dimensional supramolecular architectures. Although, the overall ligand design is very important in two-armed bridging ligands and can have a great deal of influence on the final structure of the supramolecular species so can the metal atom. Consequently, complexes containing two-armed ligands are often just as reliant on the metal atom and its geometry to enhance the complexity and sometimes dimensionality of the structure. In comparison, multi-armed ligands can bridge three or more metal atoms, thereby allowing greater connectivity and addition of another level of dimensionality into the architecture. Complexes containing multi-armed ligands are not as dependent on the metal atom to create nodes as two-armed ligands and the ligand itself can act as a coordinating node to create quite different assemblies, such as cage-like species. The literature reveals that tripodal ligands are amongst the most successful in constructing cage-like species and several types of cage-like complexes have been synthesised and fully characterised over the years. Tripodal ligands generally form cage-like species with M_3L_2 or M_6L_4 topologies.

Many reports have focused on the self-assembly of cage-like complexes with tripodal ligands based around a single benzene ring core. Some examples of these with nitrogen

heterocyclic binding arms capable of forming molecular cages with metal salts are shown in figure 4.1.[108, 200-205] Benzene ring cores are very popular as central scaffolds for molecular cages, due to the way in which one can have a 1,3,5-substitution pattern of the ligand binding arms around the ring with the arms 120° away from one another. This 1,3,5-substitution pattern around a benzene ring has proved to be a good template for the design of many tripodal ligands and several molecular cages have been generated with these ligands.

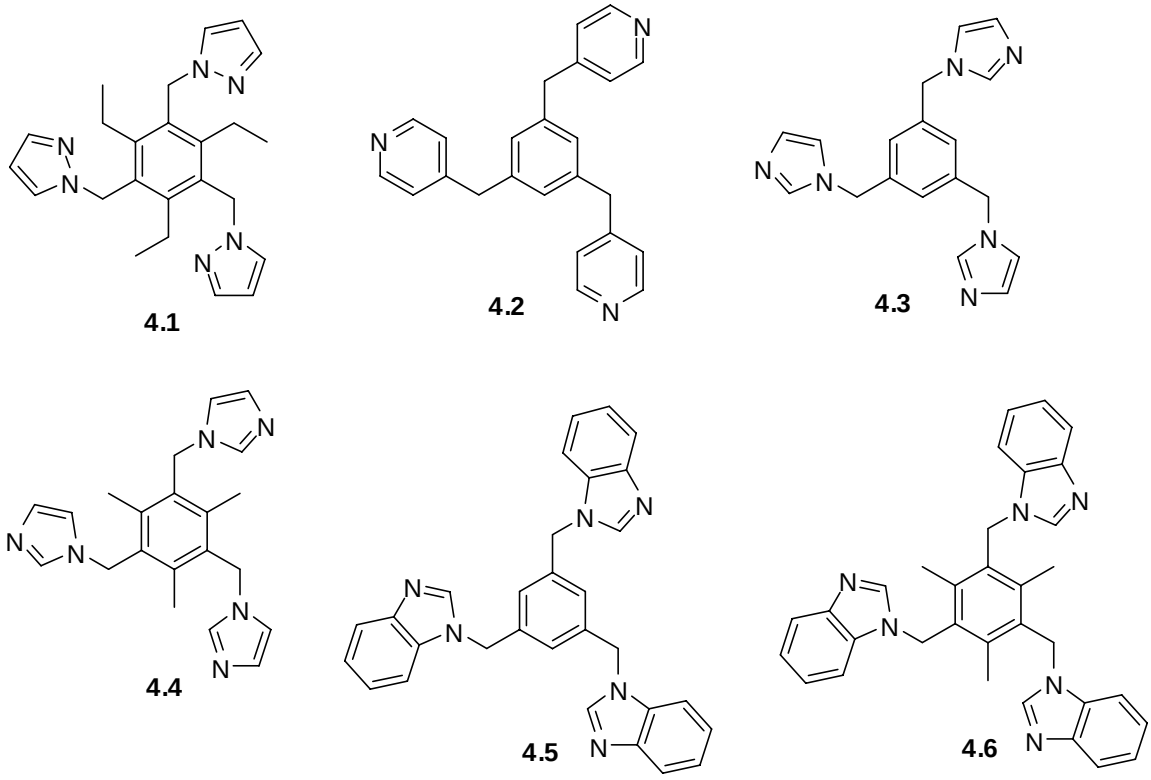


Figure 4.1 – *Some examples of heterocyclic tripodal ligands based around a single benzene ring core with the 1,3,5-substitution pattern that are capable of forming molecular cages.*

In 1995, by adopting the idea of templation, Fujita and co-workers described the self-assembly of a three-dimensional cage-like complex formed with ligand **4.2** and $Pd(en)(NO_3)_2$.[200] This fascinating five-component M_2L_3 molecular cage generated a lot of interest due to the way in which the complex spontaneously assembled in high yields in the presence of specific 'guest' molecules. The guest molecules are believed to template the self-assembly of the cage. Also in 1995, Fujita and co-workers reported the first example of a self-assembled ten-component adamantanoid M_6L_4 type cage with a

rigid trigonal ligand **4.9**, which is depicted in figure 4.3, based around a triazine aromatic core.[206] This M_6L_4 molecular cage is probably one of the most famous molecular cages in supramolecular chemistry and will be discussed in more detail in the next few pages. A couple of years later, the Steel group reported a constitutionally similar but geometrically different M_6L_4 adamantaniod cage to that of Fujita and co-workers, prepared from the flexible tripodal ligand **4.1** with $PdCl_2$.[108] It was shown that by simply varying the structure of the ligand to make it more flexible, the framework of the adamantaniod M_6L_4 cage significantly changed. This resulted in a more compact packing within the cage and hence a much smaller internal cavity.

All of the other ligands depicted in figure 4.1, **4.3-4.6**, have been shown to self-assemble into fascinating molecular cages with M_3L_2 topologies upon complexation with suitable metal salts. Some of these M_3L_2 cages contain large enough cavities to encapsulate guest molecules, which in some cases are even observed to template the formation of the cage.[200, 202, 205] A common feature shown in all the ligands illustrated in figure 4.1 is the methylene linker group that links the heterocyclic donor group to the central benzene ring. The incorporation of a methylene linker group gives the ligand extra flexibility by allowing the ligands binding arms to be able to deviate and twist away from the benzene ring plane in order to construct small cage-like assemblies.

Some other tripodal ligands based around a single benzene ring core that are capable of forming molecular cages with metal salts, are shown in figure 4.2.[207, 208] Ligand **4.7** is structurally quite similar to that of ligand **4.2**, with the only difference being the addition of a sulfur atom between the methylene linker and the 4-pyridyl groups to make it more flexible. Bray et al. reacted the tripodal ligand **4.7** with $AgNO_3$ to yield a M_3L_2 cage that had a capsule-like shape due to the inherent flexibility of the ligand binding arms and the coordination of the three silver atoms through nitrate anions.[207] The donor atom does not have to be a nitrogen atom from a heterocyclic group such as pyridine; it could also be phosphorus as in ligand **4.8**. Lindner et al. formed a M_3L_2 cage with ligand **4.8** and platinum.[208]

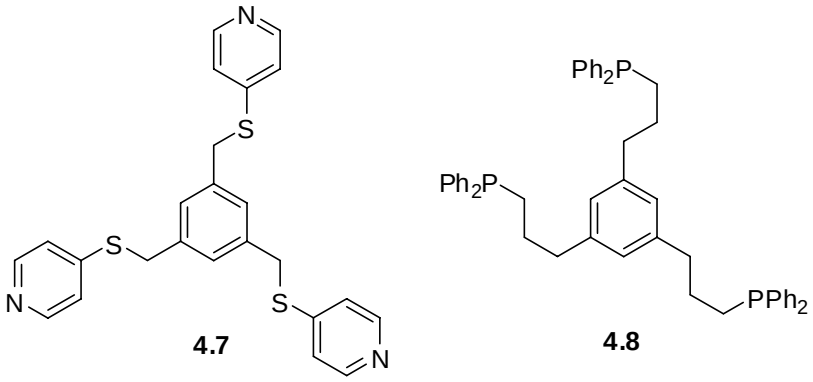


Figure 4.2 – *Two more examples of tripodal ligands that can form molecular cages.*

One is not limited to a single aromatic benzene ring as the scaffolding core for tripodal ligands. Some examples of such ligands that are based around other central scaffolding units are shown in figure 4.3. All the ligands shown in figure 4.3 are capable of forming various cage-like complexes. Ligands **4.9** and **4.10** are rigid ligands designed around an aromatic triazine core as opposed to a benzene-based central core. Both of these ligands were designed by Fujita and co-workers and self-assembled into fascinating ten-component M_6L_4 cages.[206, 209] Effectively the only difference between the triazine based ligands (**4.9** and **4.10**) and the previously discussed tripodal ligands based around a benzene ring is the absence of hydrogens on the central core. The absence of hydrogen atoms around the central ring eliminated any steric hindrance associated with the attached aromatic rings and allowed the adjoining aromatic rings to lie coplanar with the central triazine ring. The cage prepared from the tripodal ligand **4.9** was the first example of a ten-component adamantaniod M_6L_4 cage and has since become one of the most well-known and most studied molecular cages.[209-237] This self-assembled octahedral cage was obtained in quantitative yield by simply mixing together appropriate combinations of the ligand and the metal in a 2:3 ratio. What was unique about this cage was that the supramolecular framework contained a large central void in which guest molecules could be accommodated. In numerous subsequent studies Fujita and co-workers were able to demonstrate that cage-like structures with nanometer-sized cavities have the ability to encapsulate large guest molecules and chemical reactions can be carried out inside the cavity in the aqueous environment.[209-217, 219, 221, 227-237] Ligand **4.10** also self-assembles into a M_6L_4 cage from six metal ions and four tripodal ligand units and has many of the same properties as ligand **4.9**.[209]

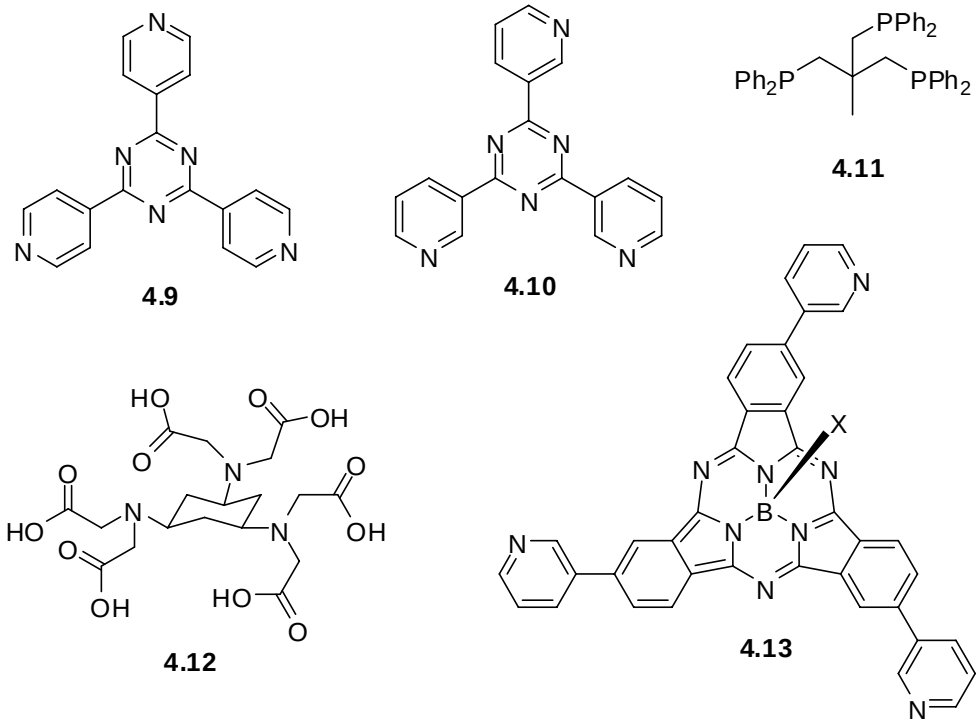


Figure 4.3 – *Examples of tripodal ligands that are based around central scaffolding units other than benzene.*

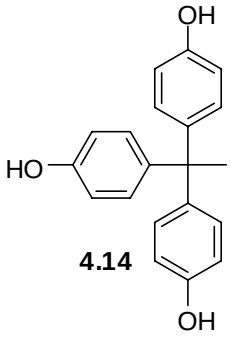
Ligand **4.11** is an example of a three-armed ligand based around just a single carbon atom. In 1998, James et al. reported the unexpected self-assembly of a M_6L_4 cage with this ligand and silver(I) cations in the presence of templating anions.[238] A while later Cooper et al. reported the formation of a M_6L_2 complex cluster with the cyclohexane-based ligand **4.12** and iron(III).[239] Ligand **4.12** has the appearance of a tridentate ligand with only three arms tethered to the cyclohexane-based core, but is actually more highly branched with a number of possible donor groups. The ligand has three tertiary amine groups and six acetate groups to coordinate to metal salts. Ligand **4.13** is quite a different ligand to all the other ligands mentioned above and is based around what is known as a 'subphthalocyanine-based' core.[240] Subphthalocyanines are fourteen π-electron aromatic macrocycles that join three nitrogen-fused diiminoisoindole units to a central boron atom. As expected with such a large system subphthalocyanines are not flat and have a curve-shaped structure to them, which makes them ideal building blocks for the formation of molecular cages with M_3L_2 topology. Claessens et al. reported the first example of a caged compound based on a subphthalocyanine-based core.

The first section of this chapter will discuss the synthesis and complexes of a new series of tripodal ligands based around a single carbon atom at the core. The family of ligands to be discussed is based around the trisphenol substituted core 1,1,1-tris(4-hydroxyphenyl)ethane. The new tripodal ligands will be reacted with various metal salts in the hope of generating complexes with interesting topologies, such as molecular cages. The rest of the chapter will discuss even larger multi-armed multidentate ligands.

Synthesis of the 1,1,1-tris(4-hydroxyphenyl)ethane based -O- spaced ligands

The majority of the tripodal ligands that have been used as building blocks for the construction of molecular cages have been designed around aromatic cores, as discussed above. Aromatic-based cores, such as benzene, provide a rigid and sturdy central core from which one can tether three evenly spaced ligand arms 120° away from one another. The intuitive design of such aromatic cored tripodal ligands has made these ligands excellent components for the construction of molecular cages. However, one is not limited to an aromatic core as the central scaffolding unit of a tripodal ligand, as previously shown in figure 4.3. Another way to make a tripodal ligand is to base the ligand core around a single atom, such as carbon. A single carbon atom is an ideal central core for the design of tripodal ligands, because one can attach three ligand binding arms off it. The fourth substituent in the terminal ancillary position can potentially be anything, such as a single hydrogen atom or a hydroxyl group. However, in this thesis the fourth substituent is a methyl group.

The structure of the trisphenol precursor 1,1,1-tris(4-hydroxyphenyl)ethane (**4.14**) is shown in figure 4.4. The precursor **4.14** can be described as a 'trisphenol', because of the three phenol substituent groups appended to the central carbon atom. The ligand precursor **4.14** consists of a central quaternary carbon atom core with a methyl group substituent in the fourth ancillary position. The trisphenol depicted in figure 4.4 is commercially available. From the trisphenol precursor **4.14** a new family of tripodal ligands was able to be synthesised and the metallosupramolecular chemistry explored.

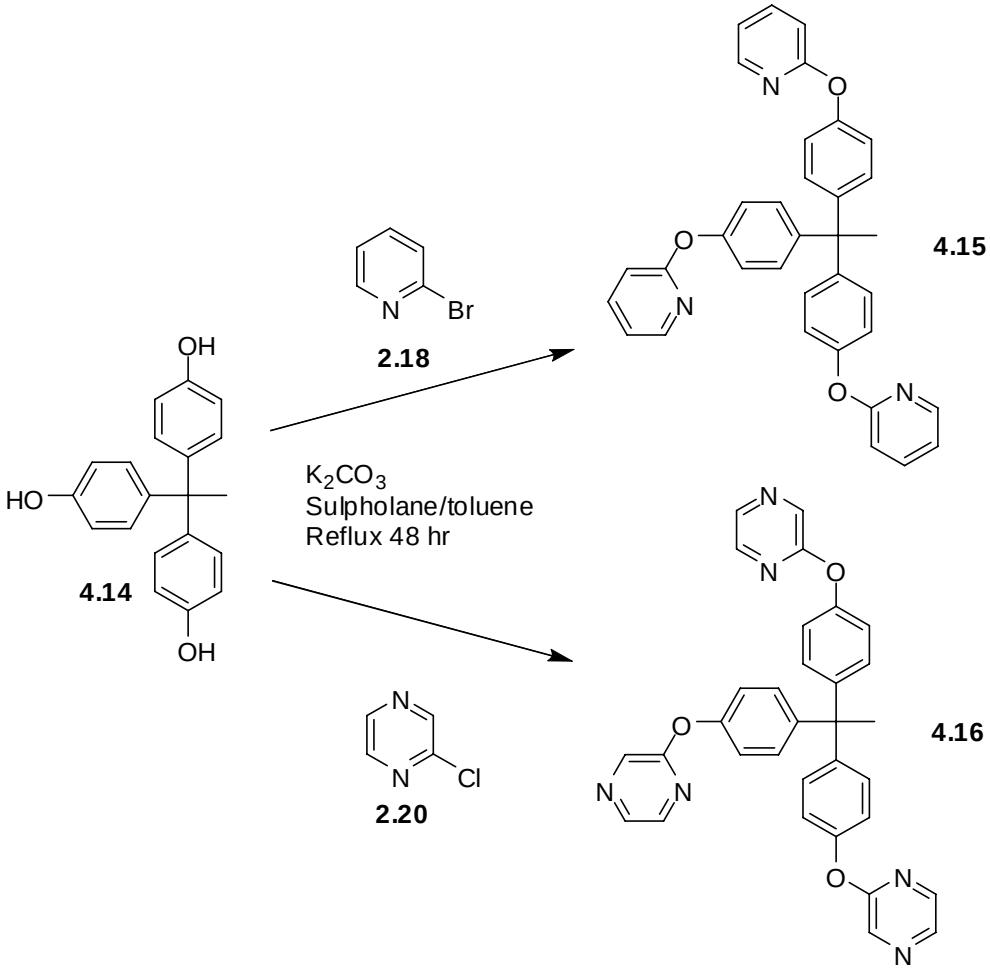


4.14

Figure 4.4 – *Structure of 1,1,1-tris(4-hydroxyphenyl)ethane.*

The first two ligands synthesised with ligand precursor **4.14** are shown in Scheme 4.1. Ligands **4.15** and **4.16** were synthesised by nucleophilic aromatic substitution of trisphenol **4.14** with the appropriate equivalents of the haloazines **2.18** and **2.20**. This synthetic route was adopted from that of O'Keefe et al. and is the same synthesis as the oxygen spaced ligands previously described in chapters two and three.[112] Both ligands **4.15** and **4.16** were recrystallised from an acetone/water solution to give yellow and white crystalline solids, respectively. Ligand **4.15** was obtained in a yield of 59% and ligand **4.16** was obtained in a good yield of 96%. Both ligands were fully characterised and the X-ray structures of both were also obtained as described below.

It is of interest to obtain the structures of some of the tripodal ligands in the solid state in order to investigate their conformations without the coordination to metal atoms, because the structure of such ligands is unknown. This can be done by analysing the overall shape of the ligand and the direction of the ligands binding arms. From this one can ascertain the potential ability of the tripodal ligands in constructing molecular cages.



Scheme 4.1 – *Synthesis of ligands **4.15** and **4.16**.*

Crystal structure of ligand 1,1,1-tris(4-(2-pyridyloxy)phenyl)ethane, 4.15

Crystals of ligand **4.15** suitable for X-ray crystallography were obtained from slow evaporation of a dichloromethane:methanol solution of the ligand. The ligand crystallises in the hexagonal space group $P6_3$ with one third of the tripodal ligand in the asymmetric unit. The central quaternary carbon, the phenyl ring and the oxygen atom of the ligand are disordered over two sites, with the major component having 75% occupancy. The crystal structure of ligand **4.15** is shown in figure 4.5, with the minor component having 25% occupancy and the hydrogen atoms not shown.

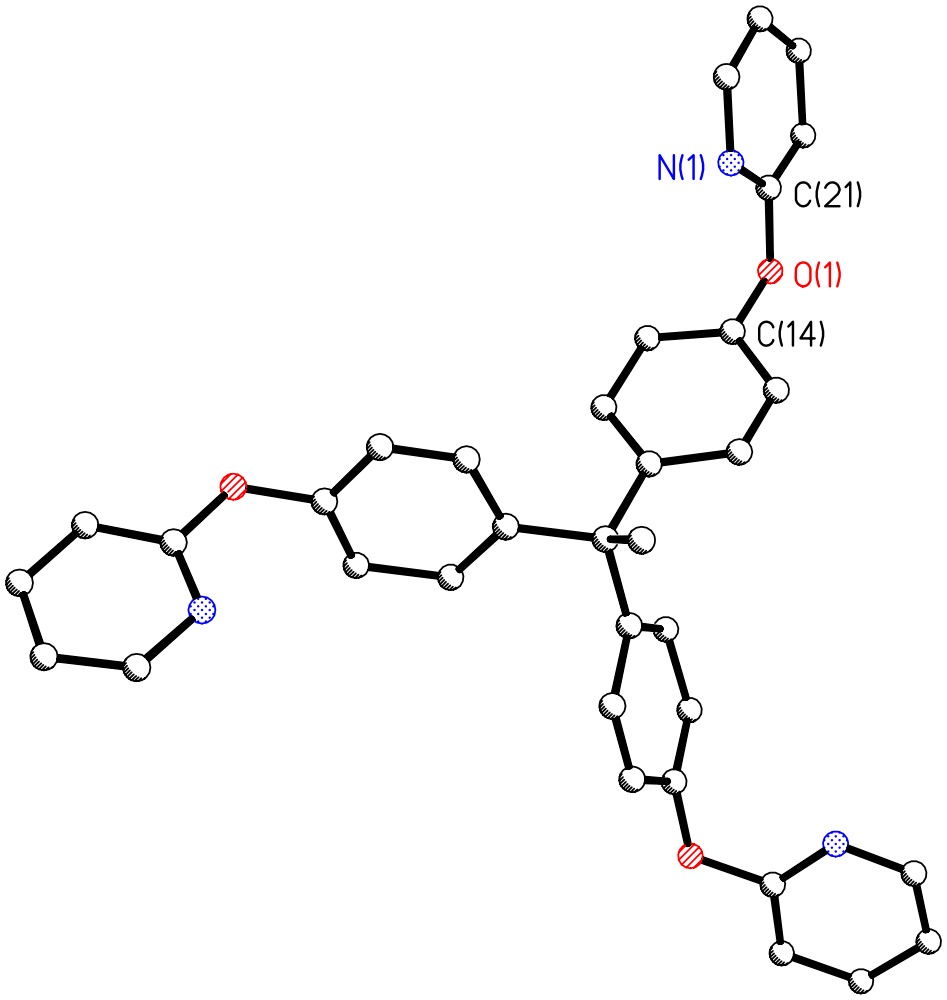


Figure 4.5 – *X-ray crystal structure of the major component of ligand* ***4.15****. Selected bond lengths (Å) and bond angles (°): C14-O1 1.415(4), O1-C21 1.397(4), N1-C21 1.319(4), C21-O1-C14 117.9(3), N1-C21-O1 121.0(3).*

In the X-ray crystal structure of the pyridine substituted ligand **4.15** the three benzene rings twist around the tetrahedral quaternary carbon atom in a propeller-like fashion with the methyl substituent pointing outwards. The three pyridine rings are tilted almost perpendicular to the mean plane of the closest benzene ring, with the internal nitrogen donor atoms all pointing inwards towards the centre of the closest benzene ring and the centre of the ligand. Ligand **4.15** has a three-fold rotation axis that passes through the central quaternary carbon of the ligand. The distance between the pyridine nitrogen atoms is 10.905Å.

In the extended structure there are edge-to-face interactions between aromatic rings as well as hydrogen bonding interactions between pyridine rings.

Crystal structure of ligand 1,1,1-tris(4-(2-pyrazinyloxy)phenyl)ethane, 4.16

Large colourless crystal blocks of ligand **4.16** were obtained by slow evaporation of an acetone solution of the ligand, suitable for X-ray crystallography. X-ray structure determination revealed the ligand to crystallise in the centrosymmetric triclinic space group P-1 with a full ligand molecule in the asymmetric unit. The crystal structure of ligand **4.16** is shown in figure 4.6, with the hydrogen atoms omitted for clarity.

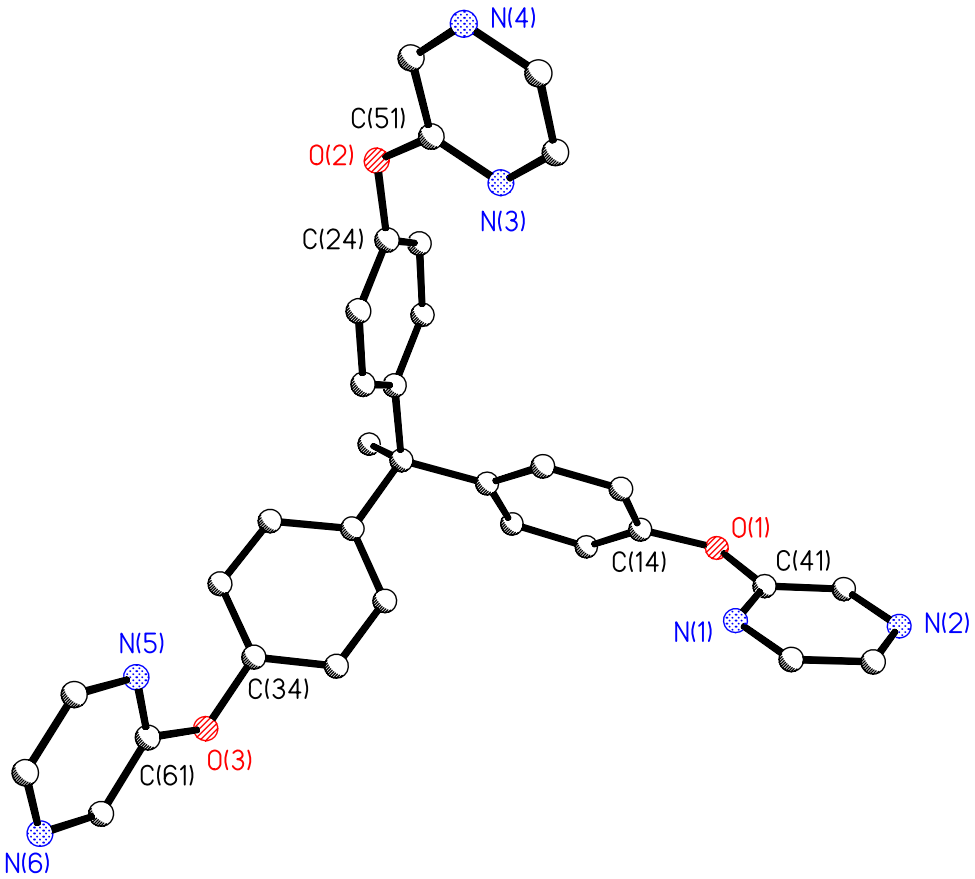
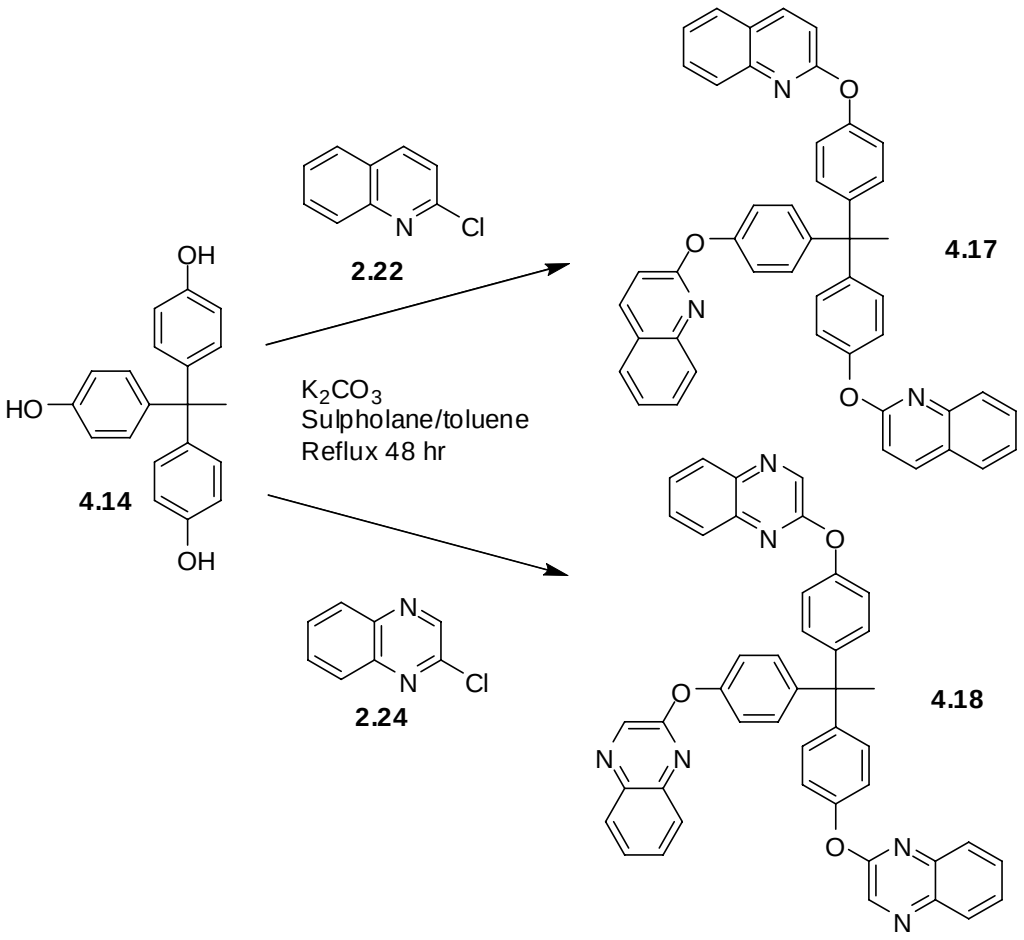


Figure 4.6 – *X-ray crystal structure of ligand* ***4.16****. Selected bond lengths (Å) and bond angles (°): C14-O1 1.416(1), O1-C41 1.374(2), N1-C41 1.317(2), C24-O2 1.419(1), O2-C51 1.366(2), N3-C51 1.317(2), C34-O3 1.421(1), O3-C61 1.366(2), N5-C61 1.319(2), C41-O1-C14 119.58(9), N1-C41-O1 120.4(1), C51-O2-C24 118.23(9), N3-C51-O2 120.7(1), C61-O3-C34 120.13(9), N5-C61-O3 121.0(1).*

In the crystal structure of ligand **4.16** the three benzene rings twist around the central quaternary carbon atom in a propeller-like array. Each of the pyrazine rings is tilted almost perpendicular to the mean plane of the attached benzene ring, with the internal nitrogen donor atoms pointing inwards towards the centre of the attached benzene rings. The external nitrogen atoms point outwards away from the central backbone of the ligand structure. As a consequence of the propeller-like twisting of the benzene rings and the conformations of the pyridyl ether groups any potential C_3 symmetry of the ligand is eliminated. Any potential internal symmetry is also destroyed in the solid state, due to the slightly different conformations adopted by the pyridyl ether units. The distances between the internal nitrogen atoms are 8.530Å (N1-N3), 9.974Å (N1-N5) and 9.643Å (N3-N5), whereas the distance between the external nitrogen donor atoms is much longer, with values of 12.783Å (N2-N4), 14.550Å (N2-N6) and 14.057Å (N4-N6). As illustrated in previous chapters, the external less hindered nitrogen donor atom is anticipated to be more likely to coordinate to metals.

The packing of ligand **4.16** is quite complex and involves many weak hydrogen bonding interactions between pyrazine nitrogens as well as numerous weak edge-to-face π interactions between aromatic rings.

The final two one-atom oxygen spaced ligands synthesised from ligand precursor **4.14** are shown in Scheme 4.2. The synthesis of ligands **4.17** and **4.18** is the same as that adopted for ligands **4.15** and **4.16** in Scheme 4.1. Both ligands **4.17** and **4.18** were also recrystallised from an acetone/water solution as yellow solids in yields of 98% and 40%, respectively. Both ligands were fully characterised by the appropriate techniques and the X-ray structures of both were also obtained.



Scheme 4.2 – *Synthesis of ligands **4.17** and **4.18**.*

Crystal structure of ligand 1,1,1-tris(4-(2-quinolyloxy)phenyl)ethane, 4.17

Colourless crystals of ligand **4.17** were grown from a mixed solution of the ligand and zinc chloride. Although the crystals were large they diffracted poorly and consequently the final structure obtained gave a large R_1 value of 22.43%. Despite this the X-ray structure of ligand **4.17** was obtained and one was able to confirm and examine the conformation adopted by ligand **4.17** in the solid state. The ligand solved in the triclinic space group P-1 with no presence of zinc chloride in the structure. One whole ligand molecule and a dichloromethane solvent molecule lie in the asymmetric unit. The asymmetric unit of ligand **4.17** is shown in figure 4.7, with the hydrogen atoms and dichloromethane solvent molecule omitted for clarity.

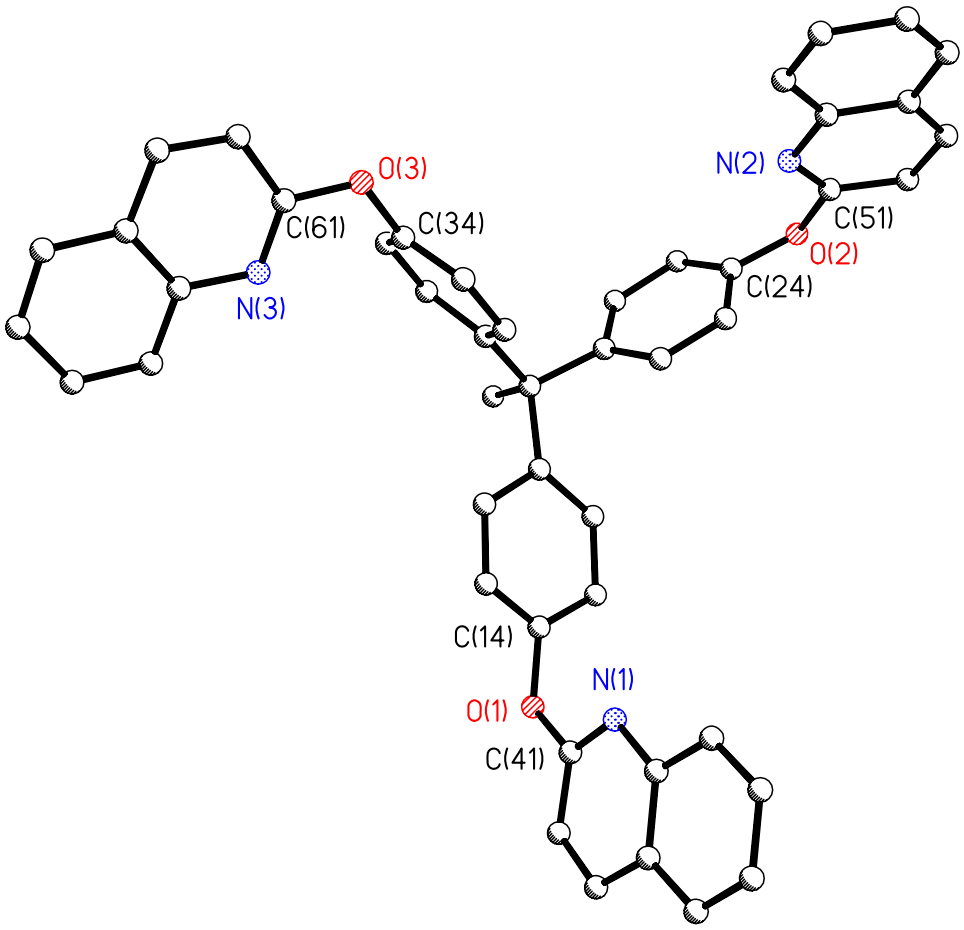


Figure 4.7 - *X-ray crystal structure of ligand* ***4.17****. Selected bond lengths (Å) and bond angles (°): C14-O1 1.434(1), O1-C41 1.374(1), C41-N1 1.308(1), C24-O2 1.400(1), O2-C51 1.405(1), C51-N2 1.292(2), C34-O3 1.428(1), O3-C61 1.373(1), C61-N3 1.346(1), C41-O1-C14 120.9(7), O1-C41-N1 118.0(9), C24-O2-C51 116.5(8), N2-C51-O2 120.4(9), C61-O3-C34 116.7(8), N3-C61-O3 117.8(9).*

Once again each of the three binding arms is tethered to a central quaternary carbon atom through a benzene ring with a methyl substituent group in the remaining fourth ancillary position. The three central benzene rings are once again splayed out in a propeller-like fashion around the central quaternary carbon atom similar to that seen in the previous tripodal ligands. The quinoline rings are facing perpendicular to the mean planes of the attached benzene rings, with the nitrogen atoms pointing inwards towards the centre of the attached benzene rings, as shown in figure 4.7. Any potential internal symmetry is once again lost in ligand **4.17**, due to the propeller-like twisting of the binding arms and the different conformations of the quinoline ether groups. The

distances between the nitrogen donor atoms are 10.366Å (N1-N2), 9.840Å (N1-N3) and 9.684Å (N2-N3), which are similar to the distances between the internal nitrogen atoms of the pyrazine substituted ligand **4.16** and in ligand **4.15**.

In the packing diagram the ligands assemble into a chain that is linked together via short contacts between the dichloromethane solvent molecules. There are short contacts between the chlorine atoms of the dichloromethane solvent molecules and quinoline rings (2.868Å and 2.875Å) and hydrogen bonding interactions between the quinoline rings (2.689Å). The ligand chains are linked to other ligand chains into sheets through more edge-to-face interactions.

Crystal structure of ligand 1,1,1-tris(4-(2-quinoxalinyloxy)phenyl)ethane, 4.18

Colourless plate-like crystals of ligand **4.18** were grown from a solution of ligand with zinc chloride. Surprisingly, once again X-ray analysis revealed a structure of just the ligand with no presence of zinc chloride. Unfortunately, the crystals were not only thin, but air sensitive as well and quickly began to decompose once removed from solvent. Although the crystal was mounted as quickly as possible in order to stop the crystal decomposing, it appears that the crystal had in fact decomposed and the diffraction patterns were weak. As a consequence, there was only enough data collected to solve the structure and an R_1 value of 22.14% was the best refinement obtained for this structure. Attempts were made to recrystallise and/or grow new crystals of the ligand without success and this data collection remains the best.

Ligand **4.18** solved in the triclinic space group P-1 with one full ligand molecule in the asymmetric unit, as shown in figure 4.8 with the hydrogens omitted for clarity. Once again the structure of ligand **4.18** in the solid state is similar to that of the previous three mentioned tripodal ligands **4.15**, **4.16** and **4.17** based around the same core. The three binding arms of the ligand are splayed out in a similar propeller-like arrangement with the quinoxaline rings perpendicular to the mean planes of the attached benzene rings. The internal nitrogen atoms are all pointing inwards towards the centre of the attached benzene rings and also directed towards the central cavity of the ligand located at the single quaternary carbon atom core. As a consequence of the propeller-like twisting of the benzene rings about the quaternary carbon atom core and the conformation of the

quinoloxaline ether groups the ligand has a concave bowl shape in which the ligand binding arms are all pointing in the same direction. Figure 4.9 shows another view of ligand **4.18** from a different direction, which clearly illustrates the bowl shape of the tripodal ligand. The ligand binding arms all wrap around the ancillary methyl group substituent group which is located in the centre of the bowl. The distances between the internal nitrogen atoms are 10.927Å (N1-N3), 10.754Å (N1-N5) and 10.867Å (N3-N5), while the distances between the external nitrogen donor atoms are much longer with values of 15.539Å (N2-N4), 15.353Å (N2-N6) and 15.501Å (N4-N6).

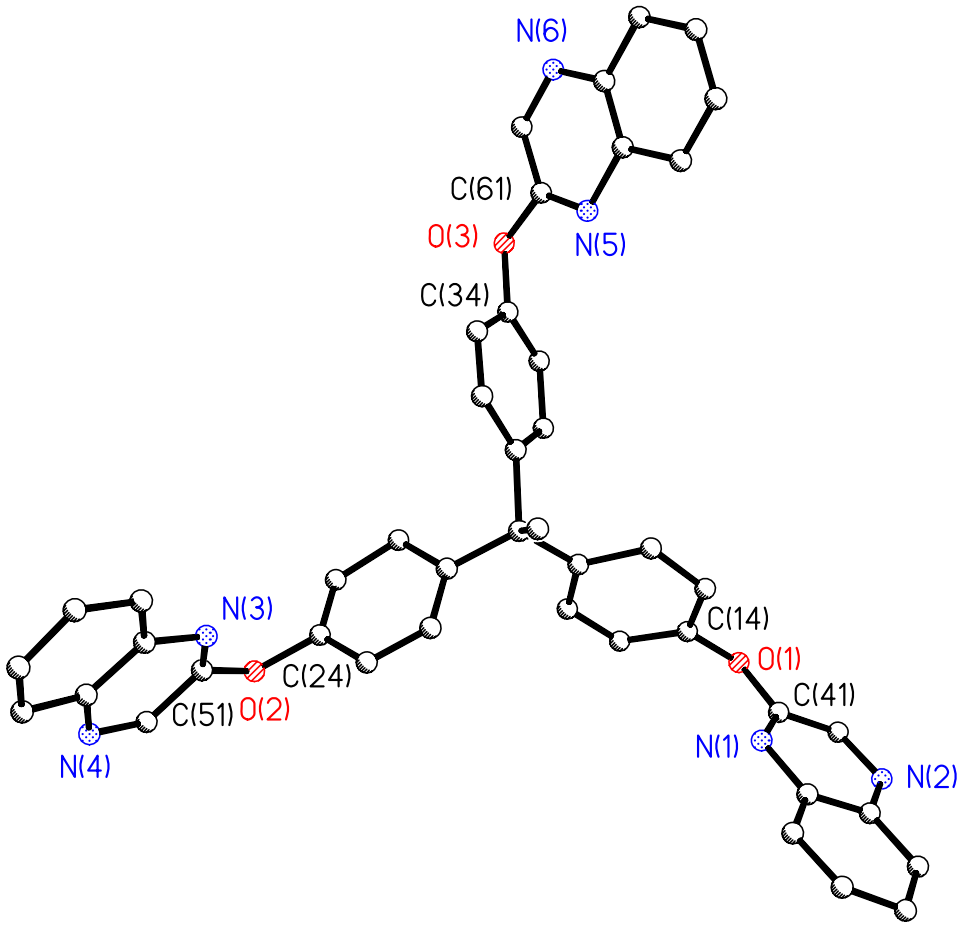


Figure 4.8 - *X-ray crystal structure of ligand* ***4.18****. Selected bond lengths (Å) and bond angles (°): C14-O1 1.426(1), O1-C41 1.407(2), N1-C41 1.293(2), C24-O2 1.494(2), O2 C51 1.377(2), N3-C51 1.284(2), C34-O3 1.463(2), O3-C61 1.407(2), N5-C61 1.306(2), C41-O1-C14 116.0(1), N1-C41-O1 122.3(1), C51-O2-C24 114.5(1), N3-C51-O2 124.0(1), C61-O3-C34 114.6(1), N5-C61-O3 120.1(9).*

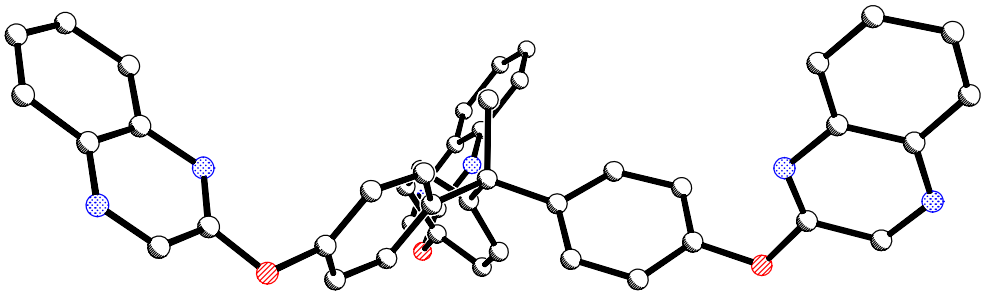


Figure 4.9 – *Another view of ligand* ***4.18*** *illustrating how the binding arms fold up around one side of the ligand creating a concave bowl shaped ligand.*

In the extended structure there are few significant interactions between ligand molecules. There are a couple of weak edge-to-face interactions between benzene rings and quinoxaline rings (2.621Å and 2.808Å), as well as hydrogen bonding interactions between the nitrogens and quinoxaline rings hydrogens (2.711Å).

A search of the literature revealed very few compounds similar to the trisphenol ligands described above. However, there are a few tripodal ligands in the literature that are also based around a single carbon atom core, which are shown in figure 4.10. Ligand **4.19** is quite similar to the trisphenol ligands with the same central core unit of a single carbon atom core with three benzene rings attached to the arms and a methyl substituent group in the fourth auxiliary position.[241] However this is the only part that is structurally similar between the trisphenol ligands and ligand **4.19**. Ligand **4.19** has two-atom flexible linkers that link the bidentate bipyridine binding domains to the central ligand core. Reaction of ligand **4.19** with ruthenium(II) produced what is known as a 'hemicage' complex.[241] A 'hemicage' complex is where all three bipyridine units coordinate to only one metal centre. Ligand **4.20** is a much smaller ligand in comparison to the other trisphenol ligands described above, due to the pyrazole arms binding directly to the carbon core.[242] There is also a benzene substituent group in the fourth auxiliary position as opposed to a methyl group. Ward and co-workers described the synthesis and reaction of this ligand with $Cu(PF_6)_2$ to give a mononuclear complex in which only two of the bidentate binding domains coordinate to the copper atom, while the other binding arm does not.[242] Ligand **4.21** is also structurally quite similar to

the trisphenol ligands with three benzene rings and a methyl substituent group tethered to a single carbon atom core with 4-pyridyl heterocyclic groups linked to the core by alkyne linkers.[243] Reaction of ligand **4.21** with platinum metal salts produced nano-sized supramolecular cages with varying sized cavities.[243] Based on this result it is hoped that trisphenol ligands will act as tritopic ligand clips with appropriate metals to create interesting supramolecular structures and hopefully cages.

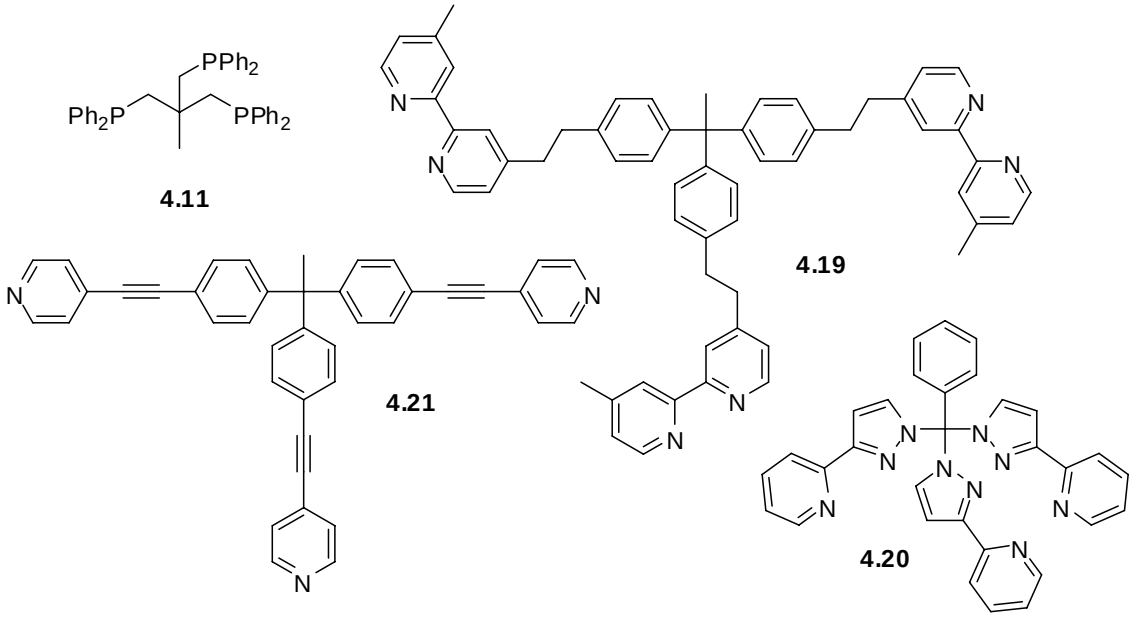


Figure 4.10 – *Structurally similar ligands to the trisphenol based ligands.*

Complexes with ligand 4.15

*Crystal structure of the complex with $CuCl_2$ (**4.22**)*

A methanol solution of cupric chloride was carefully layered upon a solution of the tripodal ligand **4.15** in chloroform. Slow evaporation of the reaction mixture over a week furnished blue/green crystals. Unfortunately the crystals were air sensitive and began to crack immediately and decompose once out of the solvent. Therefore the crystals had to be mounted and put under the cold stream of the diffractometer as quickly as possible. Unfortunately the crystals appeared to decompose within a matter of seconds; therefore it was almost impossible to mount a crystal without some decomposition. Subsequently, the diffraction patterns showed signs of the crystal being

twinned. There is also some disorder in the structure, especially in the chloroform solvent molecules. As a consequence of the crystal's rapid decomposition once removed from solvent, the disorder in the solvent molecules and twinning the structure only refines to give a poor R_1 value of over 21%. Problems with disorder and high R_1 values are quite common with large complex structures of this size. Despite this a structure solution was obtained and the crystal structure can be described.

The structure solved in the triclinic space group P-1 and X-ray analysis revealed the complex to be a fascinating five-component M_3L_2 cage. This was particularly exciting, as these tripodal ligands were originally synthesised to generate molecular cages. Examples of other tripodal ligands that are known to form molecular cages with a M_3L_2 topology have already been discussed in some detail in the introduction.

Initially, the asymmetric unit contained two M_3L_2 cages and six chloroform solvent molecules, two of which are disordered. However, it was subsequently discovered that these two were related by translation, which required halving of the a-axis. This did not improve the refinement substantially with a final R_1 value of 21.08%. A perspective view of the M_3L_2 cage is shown in figure 4.11, with the hydrogen atoms and chloroform solvent molecules excluded for clarity.

The conformation of the tripodal ligand in complex **4.22** is only slightly different to the conformation of ligand **4.15** itself in the solid state. Once again the three central benzene rings twist around the tetrahedral quaternary carbon atom in a propeller-like fashion with the methyl substituent group pointing outwards away from the cavity of the cage. In complex **4.22**, the three pyridine rings are also tilted almost perpendicular to the mean plane of the closest benzene ring, with the nitrogen donor atoms all pointing outwards away from the centre of the closest benzene ring in order to coordinate to the copper(II) atoms to form a cage-like species. This is in contrast to the conformations of the pyridyl ether units in ligand **4.15**, in which the nitrogen donor atoms were all pointing inwards towards the centre of the closest benzene ring and the centre of the ligand. As a consequence of the propeller-like arrangement of the binding arms around a quaternary carbon atom it is unlikely that the aromatic rings will align on top of another to allow π-π stacking interactions to occur.

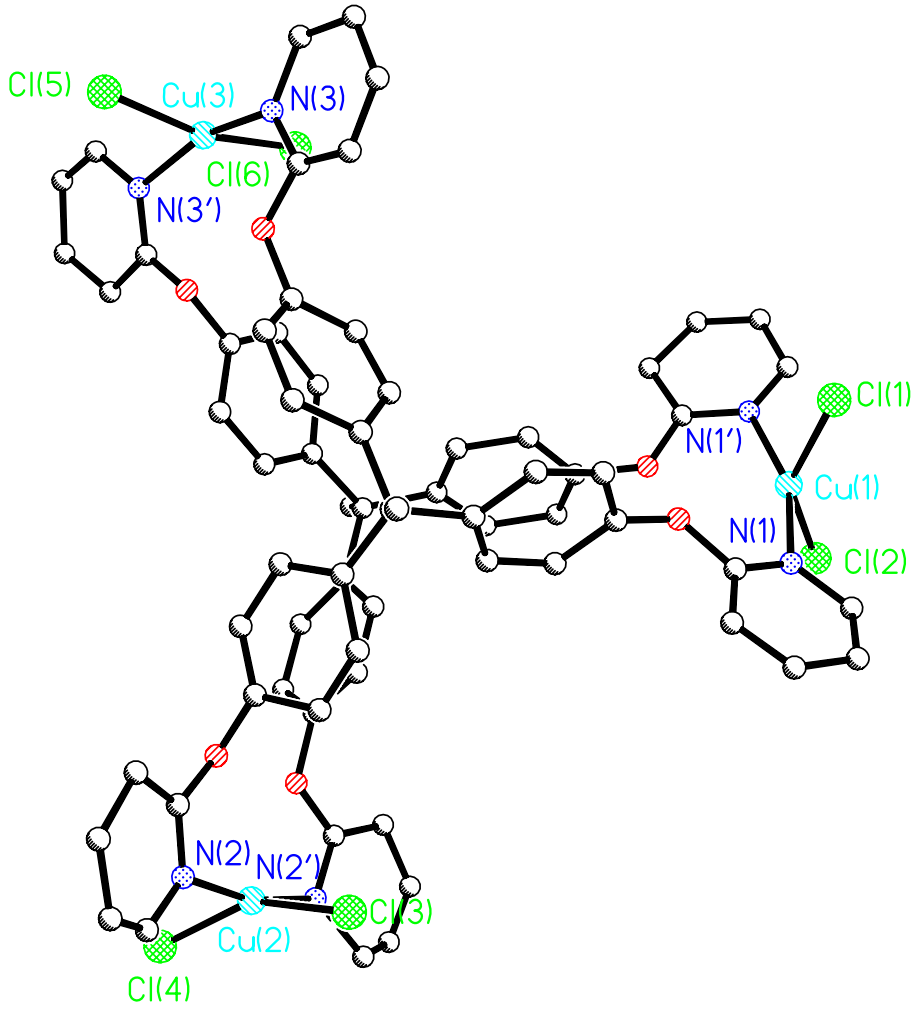


Figure 4.11 – *Perspective view of the copper chloride M_3L_2 cage when looking down through the central quaternary carbon atoms. Selected bond lengths (Å) and bond angles (°): Cu1-N1 2.01(1), Cu1-N1' 2.03(1), Cu1-Cl2 2.213(7), Cu1-Cl1 2.235(6), Cu2-N2' 1.93(2), Cu2-N2 1.97(2), Cu2-Cl4 2.245(4), Cu2-Cl3 2.270(4), Cu3-N3 1.99(2), Cu3-N3' 2.01(2), Cu3-Cl5 2.244(5), Cu3-Cl6 2.257(5), N1-Cu1-N1' 159.0(5), N1-Cu1-Cl2 93.4(5), N1'-Cu1-Cl2 94.5(5), N1-Cu1-Cl1 92.6(4), N1'-Cu1-Cl1 92.3(4), Cl2-Cu1-Cl1 144.5(2), N2'-Cu2-N2 166.7(6), N2'-Cu2-Cl4 92.1(4), N2-Cu2-Cl4 92.5(5), N2'-Cu2-Cl3 92.0(4), N2-Cu2-Cl3 89.7(4), Cl4-Cu2-Cl3 152.7(2), N3-Cu3-N3' 162.4(5), N3-Cu3-Cl5 91.2(4), N3'-Cu3-Cl5 90.6(4), N3-Cu3-Cl6 91.1(4), N3'-Cu3-Cl6 91.8(4), Cl5-Cu3-Cl6 164.8(2).*

Each of the copper atoms is 4-coordinate, binding to two pyridine nitrogens of two separate ligands and two chlorine atoms with a distorted square planar geometry. Each ligand therefore coordinates to three copper chloride centers through each of the three binding arms. The tripodal ligands in complex **4.22** both adopt *cis*, *cis*, *cis*-

conformations when joined together by the three copper(II) atoms. The tripodal ligands in complex **4.22** are flexible and therefore there are two kinds of conformations they can adopt when interacting with metal atoms. One conformation is *cis*, *cis*, *cis* and the other is *cis*, *cis*, *trans*. The *cis*, *cis*, *cis* conformation is the most commonly adopted conformation of the two in metallosupramolecular cages. The complex has pseudo C_3 symmetry. The inter-metallic distances between the copper atoms in the M_3L_2 cage depicted in figure 4.11 are 12.613Å (Cu1-Cu2), 12.695Å (Cu1-Cu3) and 14.085Å (Cu2-Cu3).

The two tripodal ligands in complex **4.22** are aligned parallel to one another through the central quaternary carbon atoms but slightly offset from one another, so that the aromatic rings cannot stack with favourable π-π interactions. The distance between the quaternary carbon atoms of the M_3L_2 cage is 6.509Å. Also as a consequence of the different conformation adopted by the ligand in complex **4.22** the pyridine rings lie approximately coplanar to one another when binding to the copper(II) centre. The coplanarity of the two pyridine rings is clearly shown in figure 4.11 and in the space-filling diagram of the M_3L_2 cage shown in figure 4.12.

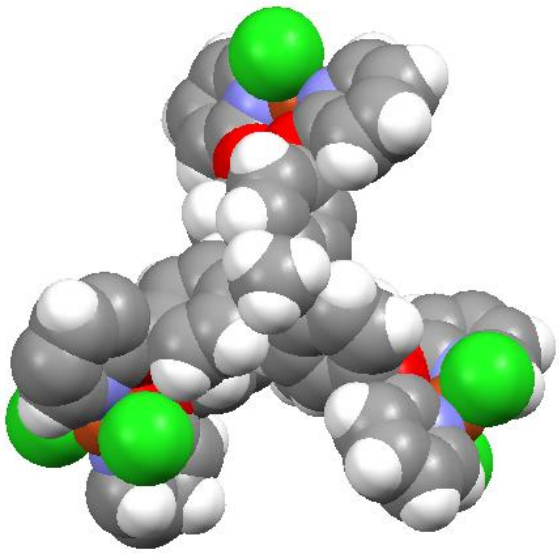


Figure 4.12 – *Space-filling diagram of the copper(II) M_3L_2 cage.*

Overall, the resulting complex is a flattened M_3L_2 cage with no central cavity, which therefore inhibits the encapsulation of any guest molecules inside the cage. The

formation of such a flattened M_3L_2 molecular cage is probably due to the propeller-like arrangement of the ligands binding arms around the quaternary carbon atom, which seem to fill in the centre of the structure. If one looks side-on at the molecular cage in a space-filling diagram one can see that there is no cavity inside the cage, as shown in figure 4.13.

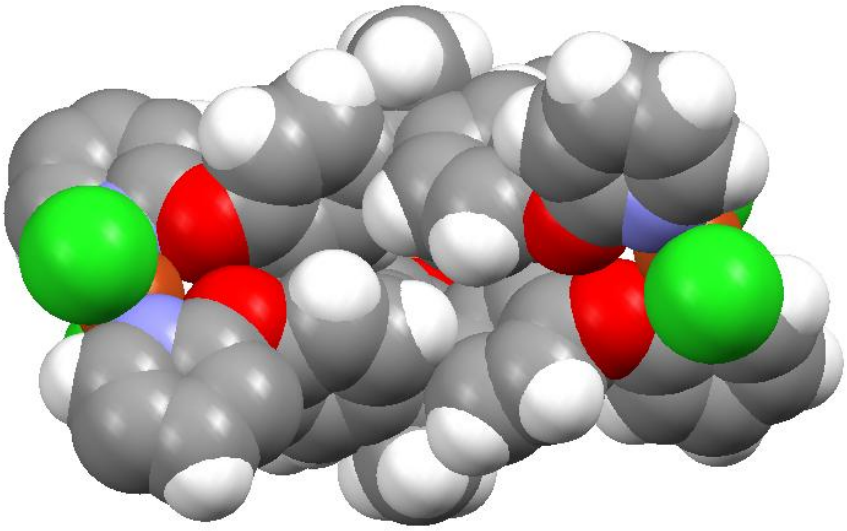


Figure 4.13 – *Side-on view of the M_3L_2 cage to illustrate that there is no cavity inside the cage as a result of the propeller-like twisting of the aromatic rings around the quaternary carbon atom.*

Interestingly, the M_3L_2 cage generated here has a similar overall shape to a couple of other copper(II) M_3L_2 cages in the literature.[244, 245] The two M_3L_2 structures in the literature were based around a 1,3,5-triphenylbenzene core as opposed to a single carbon atom in complex **4.22**. Reaction of these ligands with the copper salt $Cu(NO_3)_2$ produced M_3L_2 cages with a similar three-armed shape to **4.22**. The difference is that the cages based around the 1,3,5-triphenylbenzene based ligands have large enough cavities to encapsulate a pyridine guest molecule.[244, 245]

In the extended structure the individual M_3L_2 cages do not align and the chloroform solvent molecules fill voids between the cages in the crystal lattice through various hydrogen bonding interactions and short contacts involving the chlorine atoms. There are also some weak edge-to-face interactions between the aromatic rings of individual

cages, as well as short contacts between the chlorine atoms of each cage and adjacent cages.

Noteworthy is the fact that the elemental analysis of **4.22** verified the stoichiometry of the M_3L_2 supramolecular cage. Attempts were made to regrow and/or recrystallise the copper(II) M_3L_2 cage. Unfortunately, attempts to recrystallise the original crystals were unsuccessful. Another copper(II) M_3L_2 structure was obtained with the different solvents dichloromethane and methanol as opposed to chloroform and methanol, which crystallised with similar contents in the asymmetric unit to **4.22**. Regrettably the crystals were not strong diffractors and gave an even worse refinement than **4.22**.

*Other complexes with ligand **4.15***

The tripodal ligand **4.15** was reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(ClO_4)_2$, $Cu(NO_3)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $ZnCl_2$ and $ZnBr_2$. Only one complex was able to be crystallised and fully characterised by X-ray crystallography, as discussed above. Unfortunately, samples of other complexes were unable to be crystallised. Some of the precipitates were further analysed by elemental analysis.

Complexation of ligand **4.15** with $Cu(ClO_4)_2$ produced a blue solid on slow evaporation that analysed as a M_3L compound. This ratio could correspond to the formation of a discrete complex in which there is one copper atom coordinated to each pyridine nitrogen atom.

Reaction of ligand **4.15** with the silver salts $AgPF_6$, $AgClO_4$ and $AgCF_3SO_3$ all produced crystalline solid materials that were too small for X-ray crystallography. All of these products analysed with 1:1 ratios and are likely to be polymers.

Reaction of ligand **4.15** with $ZnBr_2$ produced a colourless crystalline solid on slow evaporation of the reaction mixture that analysed as a M_3L_2 compound. This is the correct ratio for a molecular cage complex and it could be similar to the M_3L_2 cage (**4.22**) generated with $CuCl_2$.

Complexes with ligand 4.16

*Crystal structure of the complex with CuI (**4.23**)*

The pyrazine substituted tripodal ligand **4.16** and copper iodide were both dissolved in acetonitrile and combined. Slow evaporation of the resulting pale yellow solution furnished yellow single crystals over a few weeks that were suitable for X-ray crystallography. The copper iodide complex **4.23** crystallises in the centrosymmetric triclinic space group P-1 with one ligand molecule, one CuI and a water molecule with 50% occupancy in the asymmetric unit, as depicted in figure 4.14. Excluded for clarity from the illustration are the hydrogen atoms and the water molecule.

The conformation of the pyrazine substituted ligand in complex **4.23** is similar to the conformation of ligand **4.16** in the solid state. Once again each of the three central benzene rings twists around the central quaternary carbon atom in the propeller-type arrangement. The pyrazine rings are also orientated almost perpendicular to the mean plane of the closest attached benzene ring, with the internal nitrogen atoms pointing inwards towards the centre of the attached benzene rings and the external nitrogens pointing outwards and binding to the copper atoms. As a consequence of the ligand conformation in complex **4.23** the internal nitrogen atoms are more sterically hindered and therefore do not coordinate to the copper atoms. What is interesting is that although there are three ligand arms with three binding domains, only two of the ligands arms coordinate to the copper centers, while the third ligand arm lies pendent. Effectively the tripodal ligand is acting as a two-armed bridging ligand.

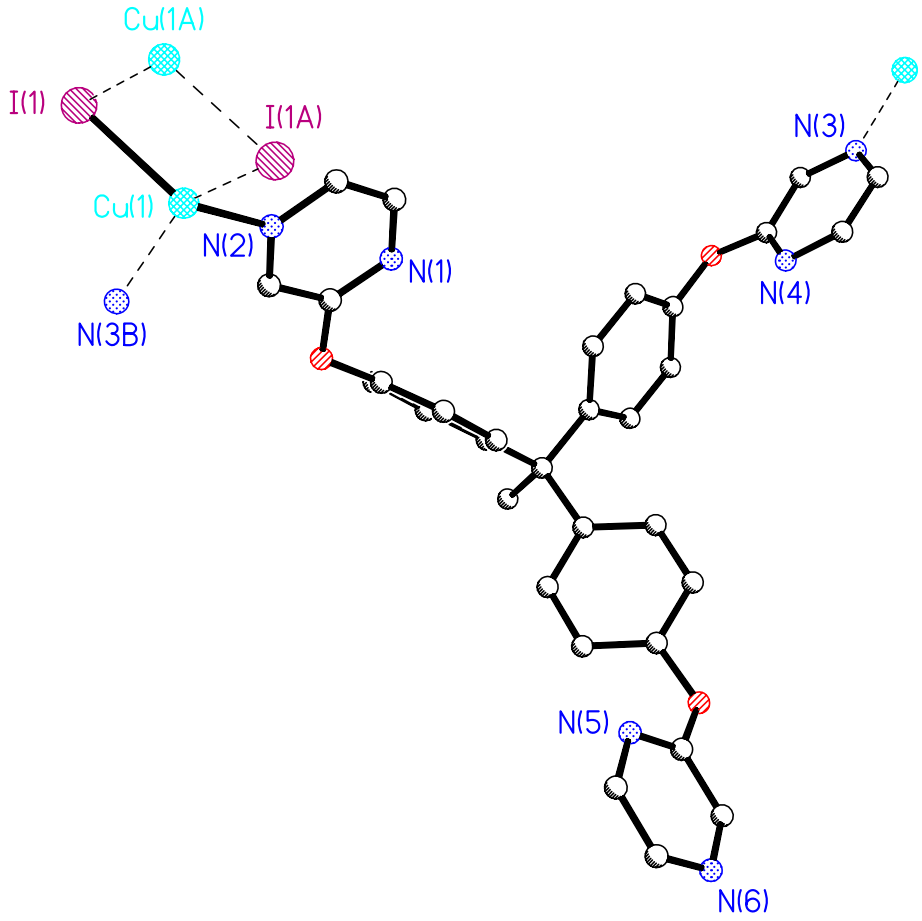


Figure 4.14 – *Contents of the asymmetric unit of complex* ***4.23****. Selected bond lengths (Å) and bond angles (°): Cu1-N2 2.043(3), Cu1-N3B 2.039(3), I1A-Cu1 2.6800(5), I1-Cu1 2.6119(5), Cu1-I1Cu1A 58.3(2), N3B-Cu1-N2 115.6(1), N3B-Cu1-I1 104.3(1), N2-Cu1-I1 110.20(9), N3B-Cu1-I1A 105.2(1), N2-Cu1-I1A 100.37(9), I1-Cu1-I1A 121.7(2).*

The copper atoms have tetrahedral coordination geometry with the largest deviation from tetrahedral arising between the two iodine atoms. Each copper atom is coordinated to two external nitrogen atoms of two separate ligands and two iodine atoms. Each copper atom is bridged by two iodine atoms to another copper atom to give a Cu_2I_2 square motif. This type Cu_2I_2 square motif has been generated many times with many of the other bisphenol ligands in this thesis. The intermetallic distance between the copper atoms is 2.578Å, which is shorter than the sum of the van der Waals radii of two copper(I) atoms (2.80Å), although the copper(I) atoms are unlikely to form a real bond.[183, 184] The Cu-N bond lengths and the Cu-I bond lengths are similar to the bond lengths of other copper iodide complexes in this thesis. In the extended structure of **4.23** each of the copper atoms coordinates to two tripodal ligands through the external

pyrazine nitrogens. Since each copper atom is part of a Cu_2I_2 motif, each Cu_2I_2 motif binds to four separate ligand molecules. The resulting complex is a double chain of M_4L_2 macrocyclic units. Figure 4.15 depicts the overall connectivity of the complex. As seen in figure 4.15 only two of the ligand arms coordinate to copper metal centers while the third arm lies pendent.

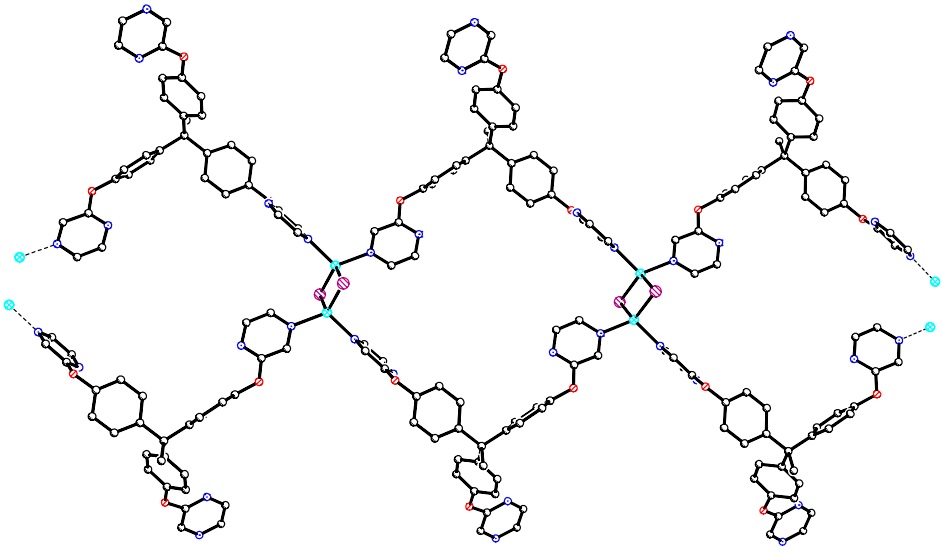


Figure 4.15 – *A section of the double chain of complex* ***4.23***.

Since only two of the ligands binding arms are coordinating to each of the Cu_2I_2 motifs the overall shape of the polymer complex is similar to some of the other necklace-like polymers generated with other two-armed bridging ligands in this thesis. Each macrocyclic unit is composed of two ligands that are coordinated to two Cu_2I_2 motifs to give a M_4L_2 macrocycle with a square-type topology in which the quaternary carbons atoms of the two ligands form two of the corners and the copper iodide square motifs form the other two. The two halves of the macrocyclic unit are related by an inversion centre. There is a large space inside each of the M_4L_2 macrocycles, which is big enough to allow for significant interactions with solvent and/or other guest molecules. The chain propagates in one-dimension being inter-linked by Cu_2I_2 motifs. As seen in many of the necklace-type polymers in this thesis the inter-linked macrocyclic units and Cu_2I_2 motifs are perpendicular to one another, as shown in figure 4.15. As a result the overall

topology of the chain is a continuous chain of large rings (the M_4L_2 macrocyclic units) linked by smaller rings (Cu_2I_2 motifs).

In the extended structure the one-dimensional necklace chains pack closely together through various significant interactions into a two-dimensional sheet. Each of the necklace chains overlaps with that of an adjacent necklace chain so that the pendent arms of the tripodal ligands are sitting inside the M_4L_2 macrocyclic cavities interacting via hydrogen bonding interactions between the non-coordinated pyrazine nitrogen atoms and aromatic hydrogens (2.542Å) to form the two-dimensional sheet. Each macrocyclic cavity unit is large enough to accommodate two pendent ligand arms; however there is no interaction between the two pendent arms. The copper iodide sheets are further linked to other sheets through hydrogen bonding interactions and other short contacts involving the iodine atoms.

*Other complexes with ligand **4.16***

The three-armed pyrazine substituted ligand **4.16** was reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(ClO_4)_2$, $Cu(NO_3)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $ZnCl_2$ and $ZnBr_2$. Once again most of the complexes gave precipitates almost immediately that were unable to be recrystallised, despite numerous attempts. As a consequence crystals suitable for X-ray crystallography were only able to be grown of one complex, as discussed above. Some of the more pure precipitates were further analysed by elemental analysis and are mentioned below.

A blue precipitate formed immediately on reaction of ligand **4.16** with $CoBr_2$ that analysed as a M_2L compound. As to be expected, this type of stoichiometry could correspond to a large number of different structures. An $AgClO_4$ complex also analysed as a M_2L compound.

White precipitates formed with two other silver salts, $AgPF_6$ and $AgCF_3SO_3$. The $AgPF_6$ complex analysed with an unusual M_7L_6 stoichiometry, which could correspond to the formation of a complex coordination polymer or much larger complex discrete structure. The $AgCF_3SO_3$ complex analysed with a 1:1 ratio.

Complexes with ligands 4.17 and 4.18

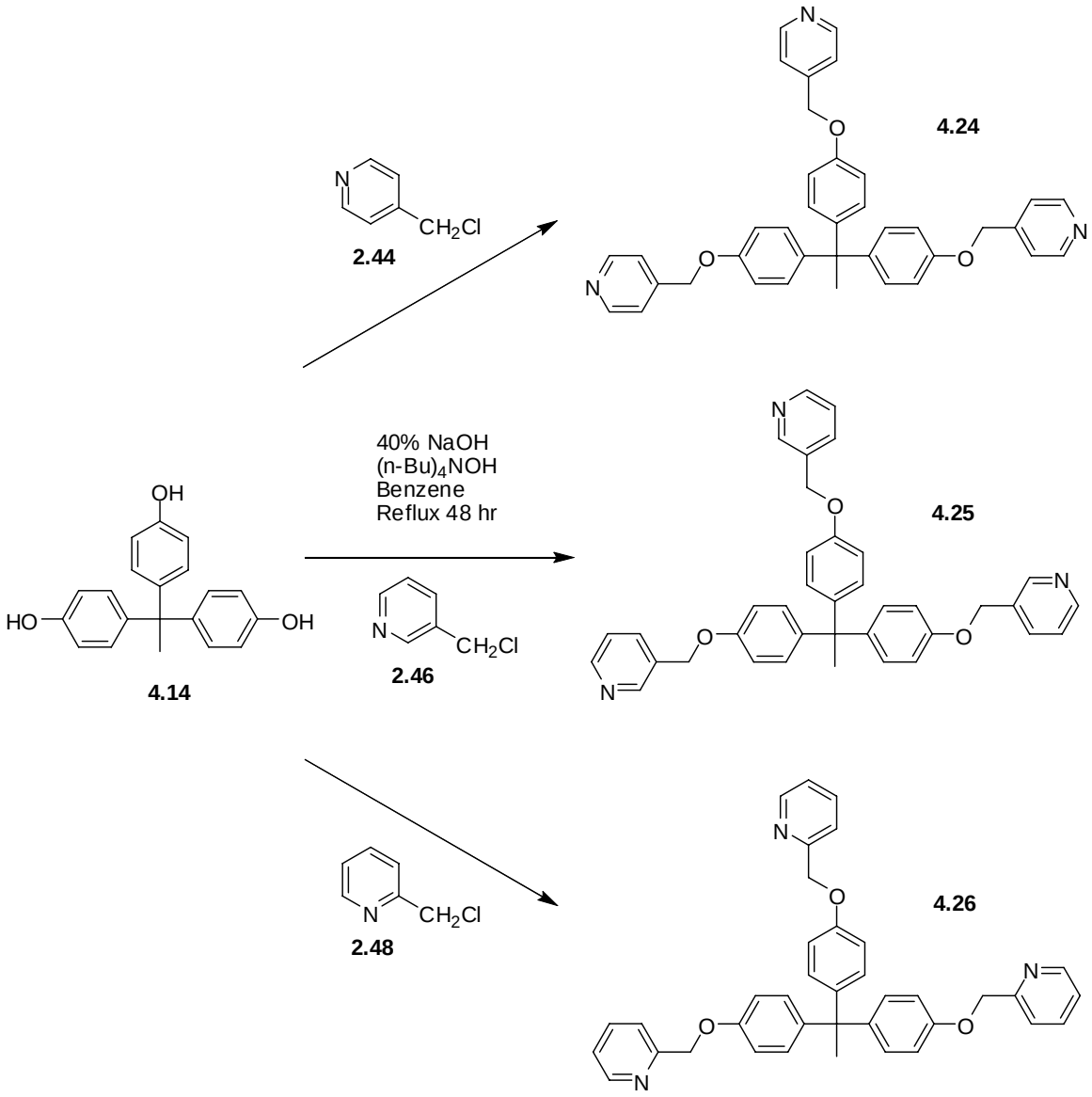
Ligand **4.17** was reacted with a large variety of the same metal salts that many of the other ligands have been reacted with. On the other hand, the quinoxaline substituted ligand **4.18** was only reacted with a selection of these due to the small amount of ligand available. Unfortunately, no crystals suitable for X-ray crystallography were obtained with either of the ligands despite several attempts to recrystallise many of the precipitates formed.

Complexation of ligand **4.17** with the silver salts $AgBF_4$, $AgClO_4$ and $AgCF_3SO_3$ produced white precipitates and a crystalline solid. Two of the products analysed as a M_3L_2 compound, which is consistent with the stoichiometry of a molecular cage. Unfortunately no crystals suitable for X-ray crystallography were obtained to validate this. Reaction of ligand **4.17** with $AgBF_4$ produced a crystalline solid that analysed as a M_2L compound.

Elemental analyses were carried out on two of the silver compounds formed with the quinoxaline substituted ligand **4.18**. Both compounds analysed with M_2L stoichiometries.

Synthesis of the 1,1,1-tris(4-hydroxyphenyl)ethane based -CH_2O- spaced ligands

Three more ligands were synthesised from the trisphenol core with a spacer group containing two atoms instead of just one to complete the series of tripodal ligands. Once again the two-atom spacer group is composed of the methyleneoxy group that is positioned between the benzene ring and a 2-, 3- or 4- substituted pyridine ring.



Scheme 4.3 – *Synthetic route to the methyleneoxy ligands **4.24**, **4.25** and **4.26**.*

The three tripodal methyleneoxy spacer group ligands were synthesised via a phase-transfer-catalysed (PTC) alkylation reaction analogous to Hartshorn et al. and is the same synthetic route used for the syntheses of other bisphenol ligands in chapters two and three.[102, 172] The ligands are outlined in Scheme 4.3. The alkylation of 1,1,1-tris(4-hydroxyphenyl)ethane with the three isomeric chloromethylpyridines gave crude ligands **4.24**, **4.25** and **4.26**. Recrystallisation of ligands **4.24** and **4.25** gave orange solids in reasonable yields of 57% and 66%, respectively. On the other hand only a 13% yield of ligand **4.26** was isolated. All three ligands were subsequently fully

characterised and the X-ray structure of the 4-pyridyl substituted ligand **4.24** was also obtained. Unfortunately, no crystal structures of any complexes with these ligands were obtained.

Crystal structure of ligand 1,1,1-tris(4-(4-pyridylmethoxy)phenyl)ethane, 4.24

Large colourless plates of ligand **4.24** were obtained by slow evaporation of a dichloromethane:methanol solution. X-ray structure determination showed the ligand to crystallise in the triclinic space group P-1. The asymmetric unit contains one whole ligand molecule and a disordered solvent molecule. The crystal structure of ligand **4.24** is shown in figure 4.16 with the disordered solvent molecule and hydrogens omitted for clarity.

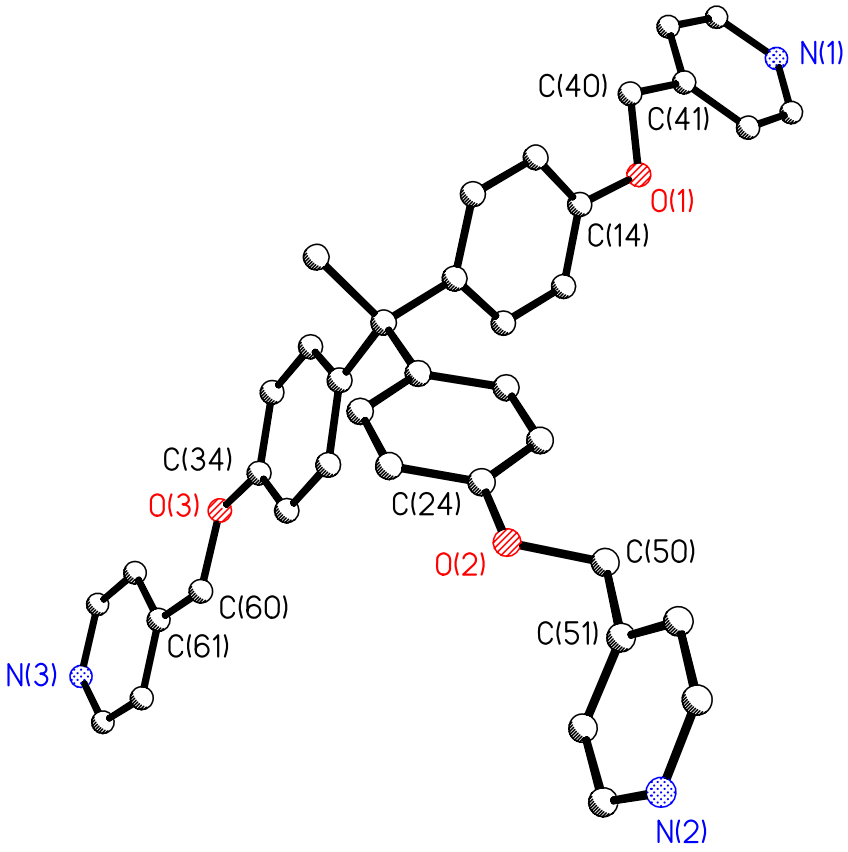


Figure 4.16 – *X-ray crystal structure of ligand* ***4.24****. Selected bond lengths (Å) and bond angles (°): C14-O1 1.382(3), O1-C40 1.438(3), C40-C41 1.511(4), C24-O2 1.380(3), O2-C50 1.442(4), C50-C51 1.498(4), C34-O3 1.384(3), O3-C60 1.423(3), C60-C61 1.499(4), C14-O1-C40 116.3(2), O1-C40-C41 107.7(2), C24-O2-C50 116.3(2), O2-C50-C51 108.0(2), C34-O3-C60 116.3(2), O3-C60-C61 110.0(2).*

The overall conformation of ligand **4.24** is quite similar to that of the previously described oxygen spaced ligands. Once again the three benzene rings and the methyl substituent group are splayed in a propeller-like fashion about the central quaternary carbon atom core, with each of the binding arms in the ligand adopting a different conformation. In two of the ligand arms, the pyridine rings lie almost perpendicular to the mean planes of the closest benzene ring, whereas in the third ligand arm the pyridine and benzene ring lie approximately coplanar with one another. All three of the nitrogen donor atoms are pointing outwards. Any potential internal symmetry is lost in ligand **4.24**, due to the propeller-like twisting of the binding arms and the different conformations of the pyridyl ether groups. The two-atom methyleneoxy spacer groups all adopt a trans-periplanar arrangement, which is reflected in the C-C-O-C torsional angles of 165.6°, 176.4° and 178.4°.

Complexes with ligand 4.24

Ligand **4.24** was reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(ClO_4)_2$, $Cu(NO_3)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $ZnCl_2$ and $ZnBr_2$. Unfortunately, no structures of complexes were crystallised and consequently many of those were not analysed any further. Some of the resulting insoluble precipitates were further analysed by elemental analysis.

Immediate precipitates formed on reaction of ligand **4.24** with most of the metal salts it was reacted with, that analysed as M_2L compounds. This stoichiometry suggests a number of possible structures. Reaction of ligand **4.24** with $Cu(ClO_4)_2$ also produced an immediate precipitate that analysed as a M_3L compound.

Complexes with ligand 4.25

Ligand **4.25** was reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(ClO_4)_2$, $Cu(NO_3)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $ZnCl_2$ and $ZnBr_2$. Most of these complexes gave immediate precipitates that were unable to be recrystallised or analysed further. However, a selection of the precipitates were analysed by elemental analysis, as discussed below.

Complexation of ligand **4.25** with $CuCl_2$ produced a green precipitate that analysed as a M_3L compound. Reaction of ligand **4.25** with $AgCF_3SO_3$ gave an immediate white precipitate that analysed with a 1:1 ratio. Elemental analysis of two other compounds produced analyses with M_3L_2 and M_7L_3 stoichiometries.

Complexes with ligand 4.26

Ligand **4.26** was only reacted with a small selection of metal salts due to the low yield of ligand initially obtained. Regrettably, no crystals suitable for X-ray crystallography were obtained with the ligand or any complexes. Reaction of ligand **4.26** with many of the many metal salts produced precipitates immediately that were insoluble. Some of the resulting precipitates were further analysed by elemental analysis.

Precipitates formed immediately on reaction of ligand **4.26** with $CoBr_2$ and $AgClO_4$ that analysed with stoichiometries corresponding to that of a M_3L_2 molecular cage. These cages could be similar to the M_3L_2 molecular cage generated with ligand **4.15** and $CuCl_2$. The only difference between the two ligands is the incorporation of a methylene group into each of the ligands binding arms of ligand **4.26**, which could potentially create more of a cavity inside the cage to encapsulate guest molecules. Unfortunately, the precipitates were unable to be crystallised to investigate this theory any further.

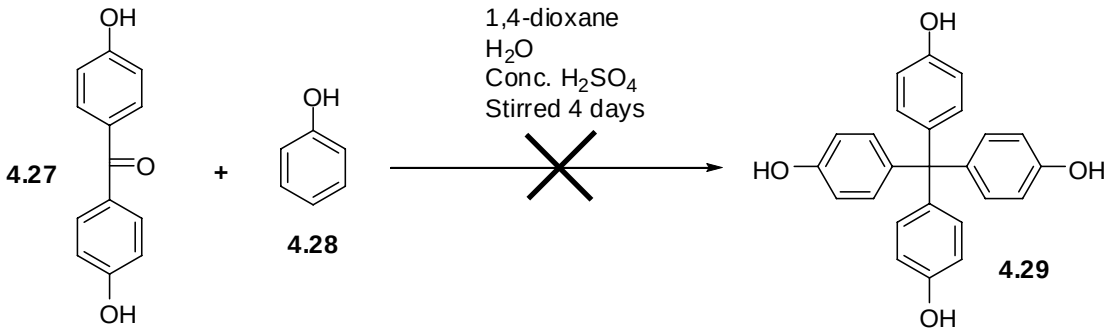
Reaction of ligand **4.26** with CuI produced a yellow precipitate immediately that analysed as a M_4L compound.

Synthesis of other multi-armed ligands

Multidentate ligands have the ability to coordinate to multiple metal atoms to construct more elaborate metallosupramolecular species than two-armed ligands. Ligands that contain more binding domains can potentially form quite large complexes with cavities that can encapsulate guest molecules and/or act as catalysts. This kind of chemistry is quite a hot topic and many groups are currently investigating a wide variety of multidentate ligands. Consequently, attempts were made to synthesis other multi-armed ligands, such as tetrapodal and hexapodal substituted ligands.

Attempted syntheses of the tetrakis(4-hydroxyphenyl)methane based ligands

Attempts were made to synthesise a tetrapodal series of ligands based around a single central quaternary carbon atom core. Four phenol groups were to be tethered off the carbon atom in order to continue with the theme of phenol substituted ligand precursors around a single atom. It would be interesting to investigate the orientation and flexibility of the ligand arms and how this would affect the overall topology of complexes. However, one must first synthesis the ligand precursor tetrakis(4-hydroxyphenyl)methane, **4.29**.

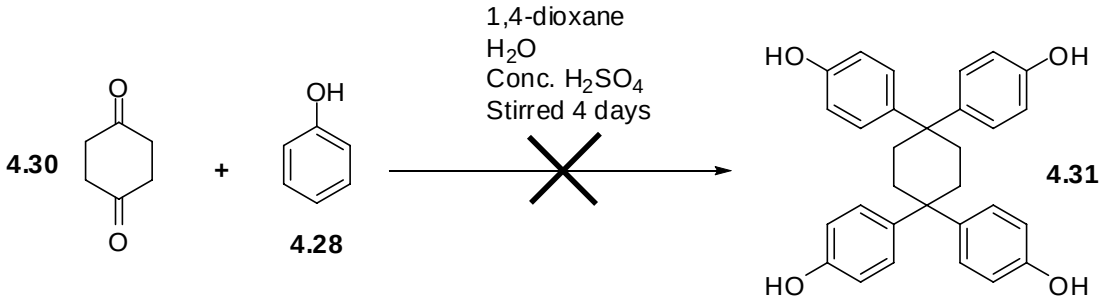


Scheme 4.4 – *The proposed synthetic route to the tetraphenol ligand precursor **4.29**.*

The proposed synthetic route, shown in Scheme 4.4, to the tetraphenol precursor **4.29** was adapted from a paper by Kolasa et al., which was previously successfully used to prepare the Bisphenol Z precursor in chapter two.[176] The synthesis involves the acid-catalysed condensation of 4,4'-dihydroxybenzophenone (**4.27**) with phenol. Unfortunately, the proposed synthesis was unsuccessful and although an orange solid was obtained, analysis by TLC and NMR revealed the supposed product to be a mixture of the two starting materials. The reaction was repeated several times with no success. It was apparent that harsher reaction conditions were needed such as those used by Wuest and co-workers when synthesising the tetraphenol **4.29** and related compounds.[246] Unfortunately, due to time constraints these were not able to be attempted.

Attempted syntheses of the 1,1,4,4-tetrakis(4-hydroxyphenyl)cyclohexane based ligands

Attempts were also made to synthesise ligands that are based around another quite different tetraphenol substituted with four arms. The proposed tetraphenol precursor **4.31** has a cyclohexane ring as the central core from which four phenol rings are coordinated in the 1- and 4-substituted positions. Attempts were made to synthesise the tetraphenol (**4.31**) via the same method employed to prepare the two-armed substituted bisphenol cores in chapter two; by reaction of 1,4-cyclohexanedione (**4.30**) with excess phenol, as shown in Scheme 4.5.[176] Unfortunately, the proposed synthesis of **4.31** was unsuccessful, due to difficulty in substituting in all four phenol groups. This reaction was tried several times; however each time the desired product was unable to be isolated.



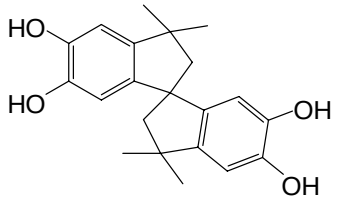
Scheme 4.5 – *The first proposed synthetic route to the tetraphenol ligand precursor **4.31**.*

A search of the literature revealed that the tetraphenol precursor **4.31** has been synthesised by more difficult methods than the one mentioned above. In a 1979 patent tetraphenol **4.31** was synthesised by reaction of a molten mixture of 1,4-cyclohexanedione and phenol with hydrogen chloride gas at 50°C until saturation was obtained.[247] A precipitate was generated that, when rinsed with methylene chloride, yielded the desired tetraphenol **4.31**. Unfortunately this reaction is fraught with the inherent problems of using hydrogen chloride gas as the catalyst. However, another literature source used concentrated hydrochloric acid as the catalyst for the condensation reaction instead of hydrogen chloride gas.[248] The use of hydrochloric acid will be better than hydrogen chloride gas and consequently this method was employed in an attempt to synthesise **4.31**.

A mixture of 1,4-cyclohexadione (**4.30**) with excess phenol was allowed to melt at approximately 50°C into a red solution. A small amount of concentrated HCl was then added to the solution to catalyse the reaction. At this point the solution changed colour to green then brown. The reaction was continuously monitored for the next few hours by TLC and then stirred overnight at a constant temperature. TLC showed the presence of the two starting materials and a potential product in the mixture. The mixture was also heavily contaminated with excess phenol; therefore most of the phenol was distilled off before continuing. The remainder of the red mixture was then treated with toluene and stirred vigorously until all the resulting precipitate had formed. It was initially thought that the precipitate obtained contained the tetraphenol **4.31** and analysis of the precipitate seemed to reveal several different products as well as some excess phenol. Attempts were made to separate and potentially identify these products by column chromatography; however no identifiable products came off the column apart from phenol. Once again this synthesis was attempted a couple more times, but with no success.

Synthesis of the 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol based ligands

Due to the limited success with the synthesis of the previous two tetraphenol precursors, another approach had to be taken in order to design and synthesise four-armed ligands. Therefore the ligand precursor 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol, **4.32**, was chosen, as shown in figure 4.17. To the best of our knowledge ligand precursor **4.32** has not been used as the central ligand core in heterocyclic ligands, although **4.32** has been used as a ligand itself in the formation of interesting metal complexes. Precursor **4.32** is commercially and cheaply available in the racemic form and therefore seemed like the ideal ligand core for a new series of heterocyclic ligands.



4.32

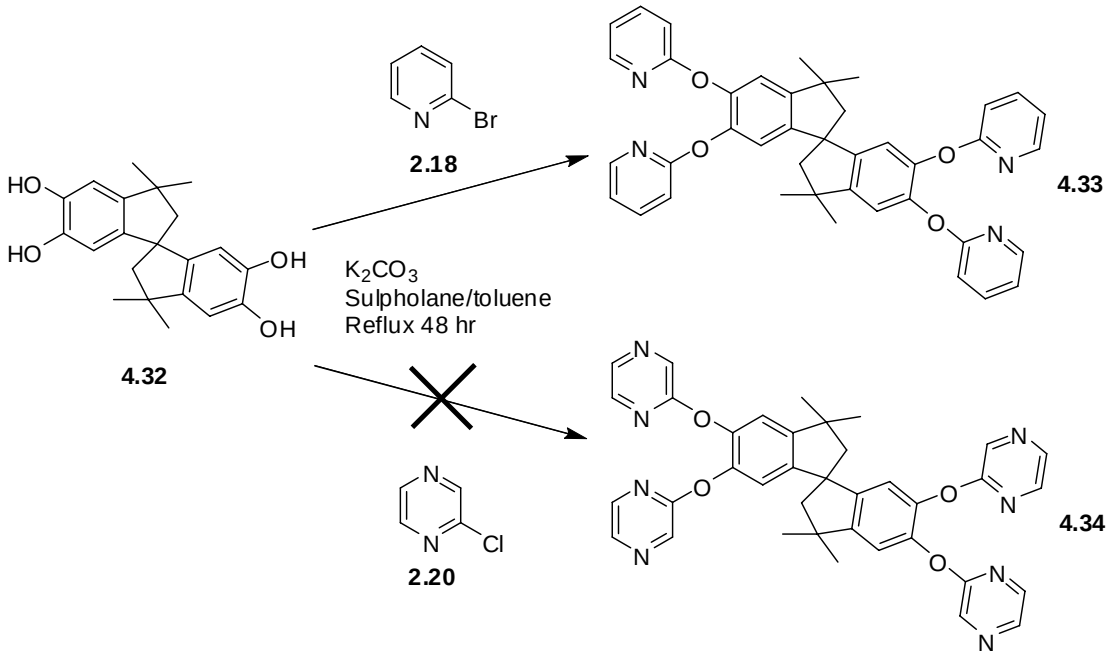
Figure 4.17 - *3,3,3',3'-Tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol.*

There are no reports in the literature of heterocyclic ligands based around a **4.32** core. However, there have been a few reports in the literature of **4.32** itself forming complexes with various metals. In 1998, Shea and co-workers reported the formation of a fascinating tetraanionic molecular square that had pentavalent siliconates from **4.32** and phenyltriethoxysilane.[249] Shea and co-workers were able to determine by NMR spectroscopy that a single diasteroisomer with C_{2h} symmetry was formed, although no X-ray structure was obtained to fully ascertain this. At around about the same time, Duhme and co-workers described the one-step self-assembly of a homochiral dinuclear molecular square with **4.32** and MoO_2^{2+}.[250] Crystals were obtained of the resulting complex thereby confirming the formation of a [2+2] dinuclear complex, although due to disordered solvent molecules and counterions the final refinement was not good. The corners of the square were defined by the two metal centers and the two orthogonal connections of the two catecholates via the spiro link. More recently, Robson and co-workers reported the synthesis of square chiral anionic macrocycles with ligand **4.32** and trimethylborate, in which each square contains four boron atoms and four molecules of ligand **4.32** with the formula $B_4L_4^{4-}$.[251] What is interesting about these molecular squares is that they stack on top of each other to generate parallel nanotubes that potentially have interesting sorption properties.

Synthesis of the 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol based -O- spaced ligands

In order to synthesis a series of heterocyclic ligands based around a 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol based core, precursor **4.32** was reacted with the same four haloazines that have been employed to generate many of the ligands

in this thesis. The first two ligands to be synthesised with precursor **4.32** are shown in Scheme 4.6.



Scheme 4.6 – *Proposed synthetic route to ligands **4.33** and **4.34**.*

Attempts were made to synthesise ligands **4.33** and **4.34** by nucleophilic aromatic substitution of precursor **4.32** with the haloazines **2.18** and **2.20**. The method adopted is analogous to that of O'Keefe et al.[112] Unfortunately, despite several attempts, the pyrazine substituted ligand **4.34** was unable to be generated and only the pyridine substituted ligand **4.33** was isolated. Ligand **4.33** was recrystallised from an acetone/water solution as a white crystalline solid in 46% yield. Subsequently, ligand **4.33** was fully characterised and the X-ray structure was obtained.

Crystal structure of ligand 5,5',6,6'-tetra(2-pyridyloxy)-3,3,3',3'-tetramethyl-1,1'-spirobisindane, 4.33.

The crude solid of **4.33** was recrystallised from an acetone/water solution. A white crystalline solid formed with clusters of colourless crystals scattered throughout. These colourless crystals were broken up into block-like crystals that diffracted perfectly for X-ray crystallography. The obtained X-ray crystal structure of ligand **4.33** is depicted in figure 4.18, with the hydrogen atoms omitted for clarity. The pyridyl-substituted ligand

4.33 crystallises in the monoclinic space group $P2_1/c$ with a full ligand in the asymmetric unit.

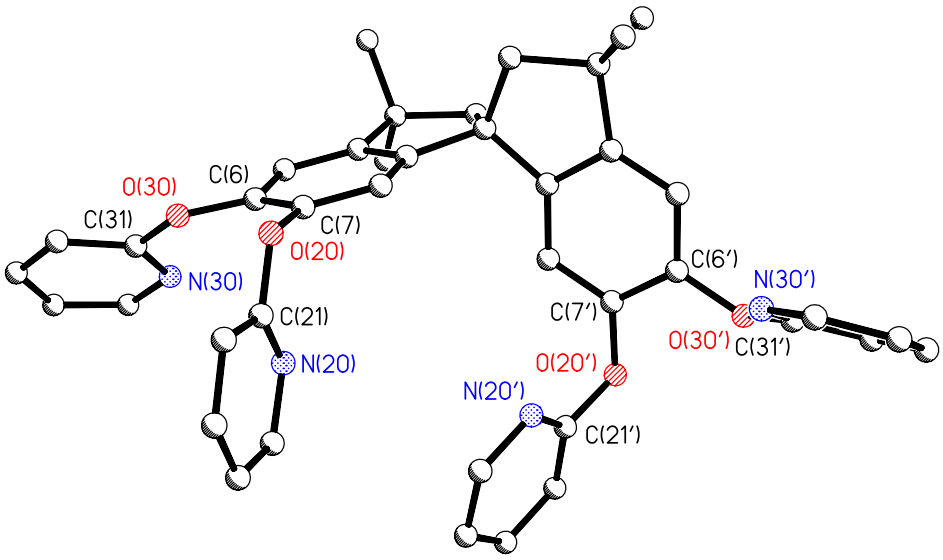


Figure 4.18 – *X-ray crystal structure of ligand* ***4.33****. Selected bond lengths (Å) and bond angles (°): C6-C7 1.394(3), C6-O30 1.388(2), C7-O20 1.401(2), O20-C21 1.367(2), N20-C21 1.333(3), O30-C31 1.375(2), N30-C31 1.315(2), C6′-C7′ 1.387(3), C6′-O30′ 1.394(2), C7′-O20′ 1.395(2), O20′-C21′ 1.375(2), N20′-C21′ 1.315(3), O30′-C31′ 1.381(2), N30′-C31′ 1.313(2), N30-C31-O30 119.7(2), C31-O30-C6 122.2(1), N20-C21-O20 120.7(2), C21-O20-C7 117.2(1), C6-C7-O20 119.64(16), C7′-C6′-O30′ 117.4(2), C6′-C7′-O20′ 118.7(2), N20′-C21′-O20′ 118.6(2), C21′-O20′-C7′ 117.7(1), N30′-C31′-O30′ 118.4(2), C31′-O30′-C6′ 119.3(1).*

There is no internal symmetry in ligand **4.33**. The two catecholate ring planes of ligand **4.33** are oriented almost orthogonal to one another and are connected via a spiro carbon junction. The four pyridyl ether groups, two off each catecholate ring, are all oriented almost perpendicular to the mean plane of the closest catecholate ring. Two of the nitrogen donor atoms that are positioned on the pyridyl groups of the same catecholate ring are pointing outwards in one direction, while the other two nitrogen donor atoms are pointing in the opposite direction. This can be seen more clearly in the space-filling diagram shown in figure 4.19. The direction that the nitrogen donor atoms of the pyridyl groups point is a consequence of the rigid angular chiral shape of the spiro ligand. The angular conformation of ligand **4.33** is particularly suited for the formation of molecular squares, due to the spiro center acting as an angular component to form the

corners of the square. Thus with the combination of the appropriate metal center more elaborate and interesting supramolecular structures might be generated.

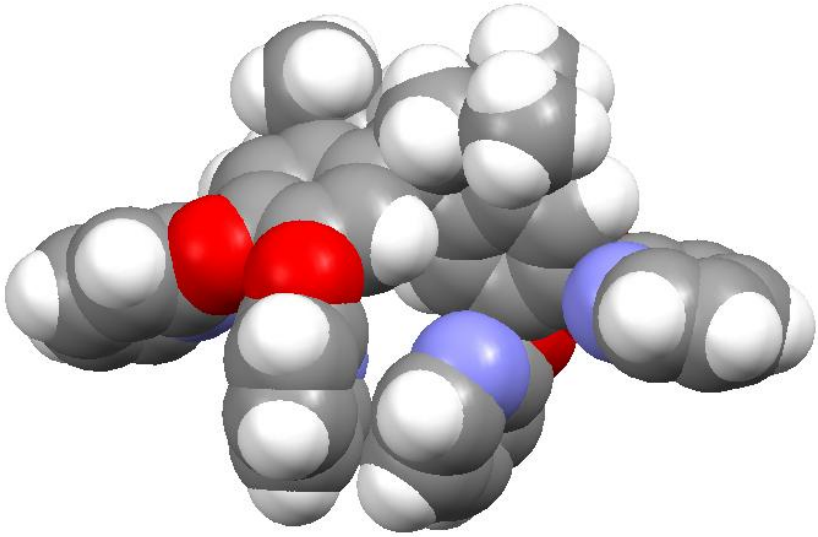
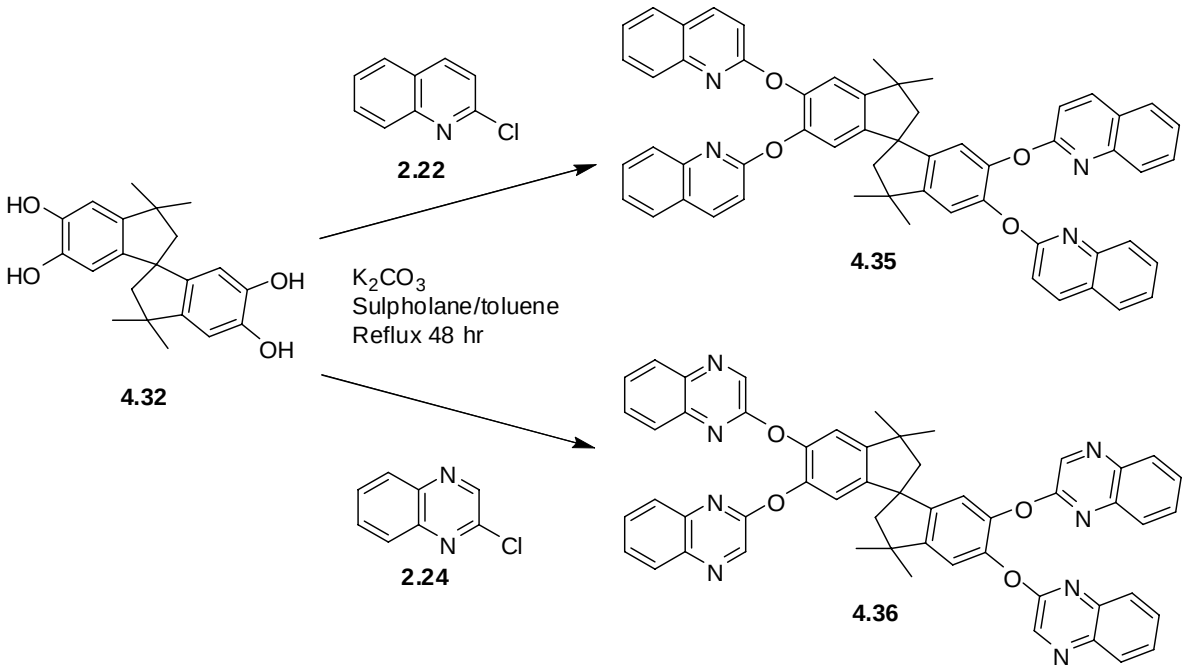


Figure 4.19 – *Space-filling diagram of ligand* ***4.33****, which more clearly illustrates the orientation of the 2-pyrdyl groups, due to the rigid conformation of the spiro ligand.*

The next two ligands synthesised from precursor **4.32** are outlined in Scheme 4.7. New ligands **4.35** and **4.36** were synthesised in an analogous reaction to that shown in Scheme 4.6 with the larger haloazines 2-chloroquinoline (**2.22**) and 2-chloroquinoxaline (**2.24**). Recrystallisation of crude ligands **4.35** and **4.36** in an acetone/water solution produced yellow solids in modest yields of 64% and 54%, respectively. Subsequently, these ligands were fully characterised and an X-ray structure of **4.35** was acquired.



Scheme 4.7 – *Synthesis of ligands **4.35** and **4.36**.*

Crystal structure of ligand 5,5',6,6'-tetra(2-quinolyoxy)-3,3,3',3'-tetramethyl-1,1'-spirobisindane, 4.35.

Colourless block-like crystals of ligand **4.35** were grown from a solution of ligand **4.35** and cobalt bromide. The compound crystallises in the orthorhombic space group Pnn2 with half a ligand molecule in the asymmetric unit. The X-ray structure of the full ligand molecule of **4.35** is shown in figure 4.20, with the hydrogen atoms omitted for clarity.

The central core of ligand **4.35** is similar to that of the previously described pyridine substituted ligand **4.33**. The two catecholate ring planes, which are connected via a spiro carbon junction, are almost orthogonal to one another. The nitrogen donor atoms of the quinoline ether heterocyclic groups are once again facing outwards, but also slightly orientated towards the centre of the closest benzene ring of the catecholate group. The two nitrogen donor atoms of the quinoline rings off the same catecholate ring are facing in one direction, while two nitrogen donor atoms of the other quinoline rings are facing in the opposite direction.

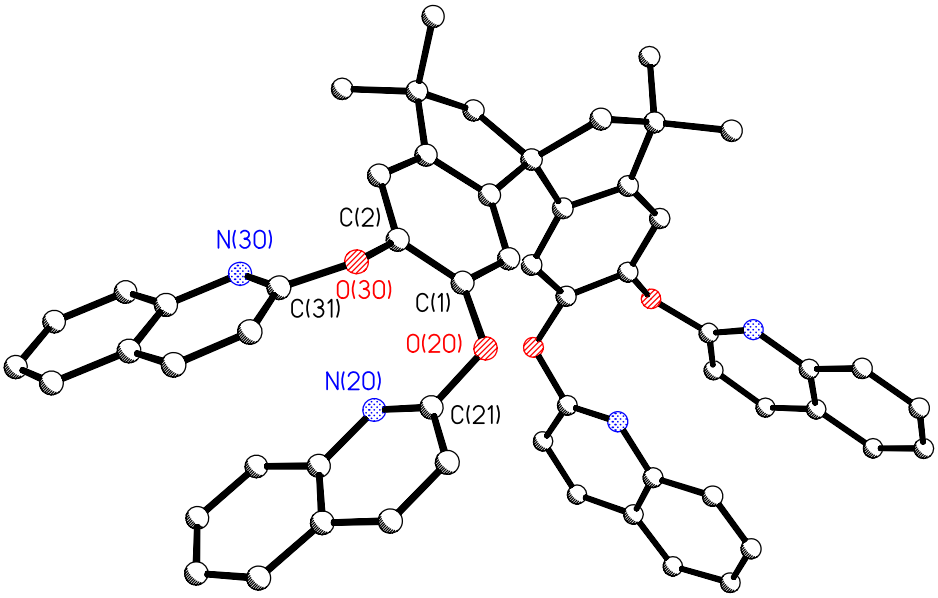


Figure 4.20 - *X-ray crystal structure of ligand* ***4.35****. Selected bond lengths (Å) and bond angles (°): C1-C2 1.395(3), C1-O20 1.394(2), C2-O30 1.394(2), O20-C21 1.374(2), C21-N20 1.292(2), O30-C31 1.375(2), C31-N30 1.292(2), C2-C1-O20 121.4(2), C1-C2-O30 116.9(2), C21-O20-C1 118.1(1), N20-C21-O20 119.2(2), C31-O30-C2 120.6(1), N30-C31-O30 121.1(2).*

In the extended structure the ligand molecules pack together with interactions between them. There is however a weak edge-to-face interaction between the quinoline rings of adjacent molecules (2.694Å).

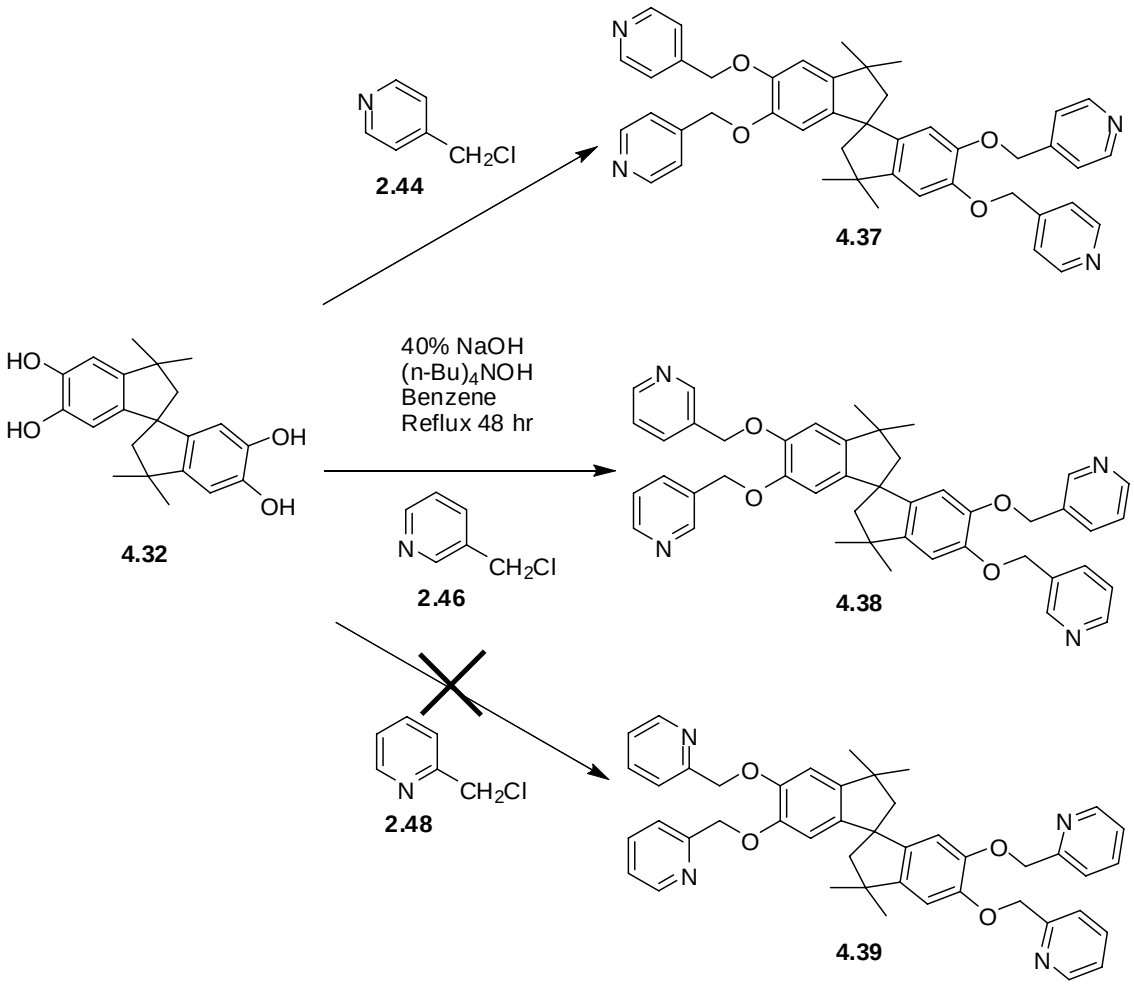
All three 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol based ligands **4.33**, **4.35** and **4.36** were reacted with a variety of different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(ClO_4)_2$, $Cu(NO_3)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $ZnCl_2$ and $ZnBr_2$ in the hope of constructing new and unique metallosupramolecular species. A large number of complexes were made with all three of these ligands, but unfortunately no complexes were able to be crystallised. Most of the complexes that formed were precipitates that were subsequently unable to be recrystallised. Some of the precipitates were further analysed by elemental analysis and are listed in more detail in the experimental section.

Synthesis of the 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol based -CH_2O- spaced ligands

Three more ligands were synthesised from the 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol, **4.32**, with a spacer group containing two atoms, instead of just one. The spacer group adopted was a methyleneoxy group that is positioned between the catecholate rings and a 2-, 3- or 4-substituted pyridine ring.

The three ligands synthesised from precursor **4.32** with a two-atom spacer group are outlined in Scheme 4.8. Ligands **4.37**, **4.38** and **4.39** were synthesised via an analogous phase-transfer-catalysed (PTC) alkylation reaction to that shown in Scheme 4.3 earlier. The quadruple alkylation of precursor **4.32** with two of the chloromethylpyridines gave crude ligands **4.37** and **4.38**. Regrettably, ligand **4.39** was unable to be synthesised, despite several attempts. Ligand **4.37** was recrystallised from petroleum ether/ethyl acetate as a yellow solid in 34% yield. Ligand **4.38** was isolated as a white solid in 33% yield after flash chromatography and recrystallisation from an acetone/water solution. Subsequently, both of these ligands were fully characterised.

Ligands **4.37** and **4.38** were also reacted with a wide variety of metal salts, similar to that listed with the oxygen spaced 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol based ligands. Once again a number of complexes were made with both these ligands, however no complexes were subsequently crystallised. Most of the complexes that formed with both the ligands were precipitates that were insoluble in common solvents, making it impossible to crystallise any of them. Some of the precipitates obtained were analysed by elemental analysis and are listed in more detail in the experimental section.



Scheme 4.8 – *Proposed synthetic route to ligands **4.37**, **4.38** and **4.39**.*

Synthesis of the hexasubstituted dipentaerythritol based ligands

Many six-armed ligands have been designed and synthesised around various aromatic ligand cores. The Steel group has also synthesised a number of such ligands, a selection of which are depicted in figure 4.21.[252-255] Larger multi-armed ligands can potentially generate more complex metallosupramolecular arrays, due to the greater number of binding domains.

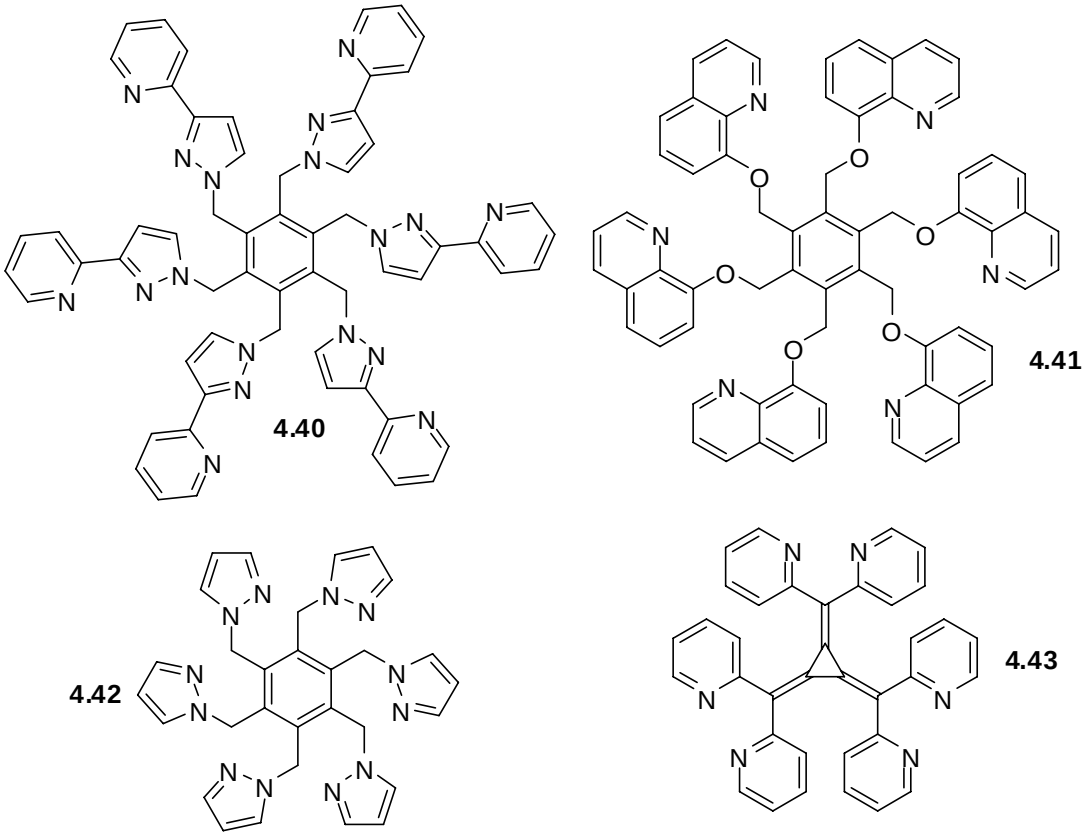
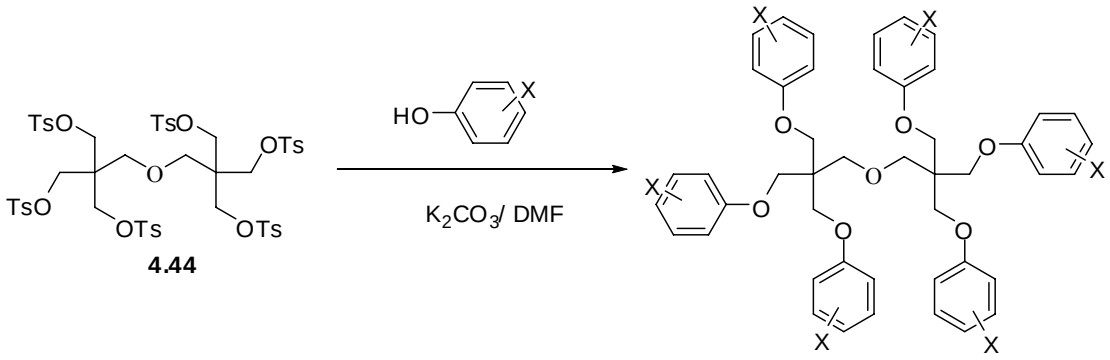


Figure 4.21 – *A few examples of hexasubstituted ligands that have been synthesised by previous members of the Steel group.*

Three of the hexasubstituted ligands depicted in figure 4.21 are based around a single benzene ring.[252, 254, 255] A single benzene ring is a good central scaffolding unit for the formation of six-armed ligands, due to the way in which it promotes the substituent groups to arrange themselves in an alternating manner around the ring so that the substituent groups are on alternating faces of the ring. One is not just limited to a single benzene ring as the central core for hexasubstituted ligands and other interesting cores can be adopted. Ligand **4.43** is one example of such a core.[253] Sumby et al. used ligand **4.43**, which is composed of a [3]radialene group as the central scaffolding unit with 2-pyridyl substituent groups appended to it. Reaction of these hexasubstituted ligands with various metal salts has produced some very exciting complexes. One particular complex that stands out is the M_6L_2 cage generated from ligand **4.43** and $AgBF_4$.[253]

Many other cores have been adopted in the design and construction of hexasubstituted ligands. One such ligand core is dipentaerythritol. In 2003, Wuest and co-workers synthesised a diverse range of hexasubstituted derivatives of dipentaerythritol

hexaphenyl ether.[256] These ligands were conveniently synthesised in two steps. The first step involved the reaction of various phenols with the ligand precursor dipentaerythritol hexatosylate (**4.44**) to form a variety of new six-armed ligand derivatives, as shown in Scheme 4.9. The X substituent groups, which are not shown here, could be Br, NO_2, CN or CHO substituent groups.[256]



Scheme 4.9 – *Reaction scheme towards the synthesis of hexasubstituted ligands based around a dipentaerythritol core.*

In step two, the new hexasubstituted derivatives of dipentaerythritol hexaphenyl ether underwent further reactions to form a variety of six-armed ligands. Wuest and co-workers discuss one ligand in particular, **4.45**, as shown in figure 4.22, which was synthesised by the reaction of the hexanitrile with dicyandiamide under standard conditions.[256] Ligand **4.45** was prepared in good yield and crystals were grown suitable for X-ray crystallography. X-ray analysis of ligand **4.45** showed that the hexasubstituted ligand self-associates by extensive hydrogen bonding of its diaminotriazine groups to form an extended three-dimensional network with significant volume for the inclusion of guests.

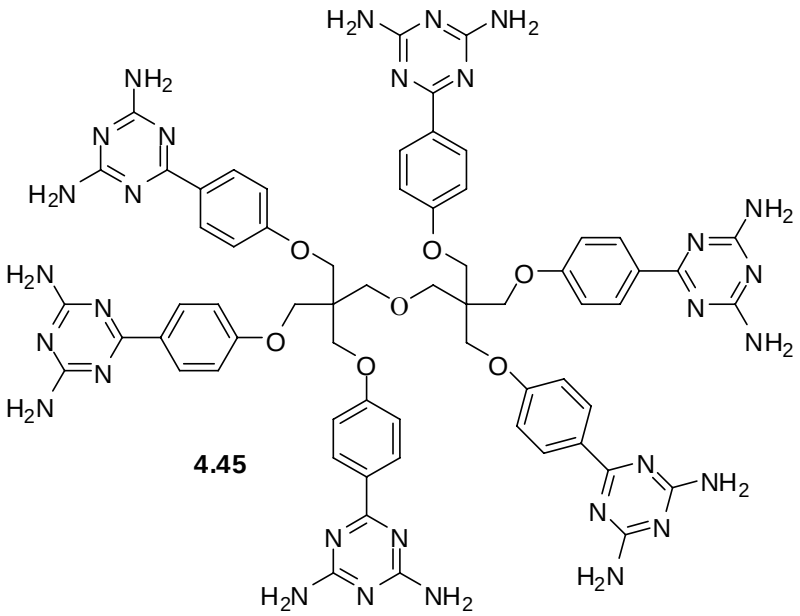


Figure 4.22 – *The hexasubstituted ligand designed by Wuest and co-workers.*[256]

A few other examples of compounds based around a dipentaerythritol unit are depicted in figure 4.23. Wuest and co-workers also designed and synthesised a few other dipentaerythritol based compounds, such as compound **4.46**.[257] Compound **4.46** also displayed an extensive hydrogen bonded network in the solid state. In 2003, Nättinen and Rissanen synthesised a couple of dipentaerythritol-based pyridinate compounds, **4.47** and **4.48**, that also displayed hydrogen bonded networks in the solid state.[258] Nättinen and Rissanen mentioned that they had some difficulty crystallising the dipentaerythritol-based pyridinate compounds due to the bulkiness of the substituent groups and the flexibility of the structure. Not long after this Pike et al. described the synthesis of compound **4.49**.[259] Reaction of this with Mn(I) and Cu(I) gave a discrete bimetallic complex with Mn(I) and a polymeric network with Cu(I) showing the versatility of compound **4.49** as a bridging ligand.[259] Although there have been a few dipentaerythritol-based compounds synthesised few have been reacted with metal salts. Therefore it is of great interest to synthesise dipentaerythritol-based compounds with six nitrogen heterocyclic groups suitably positioned for the bridging of metal atoms with varying degrees of separation.

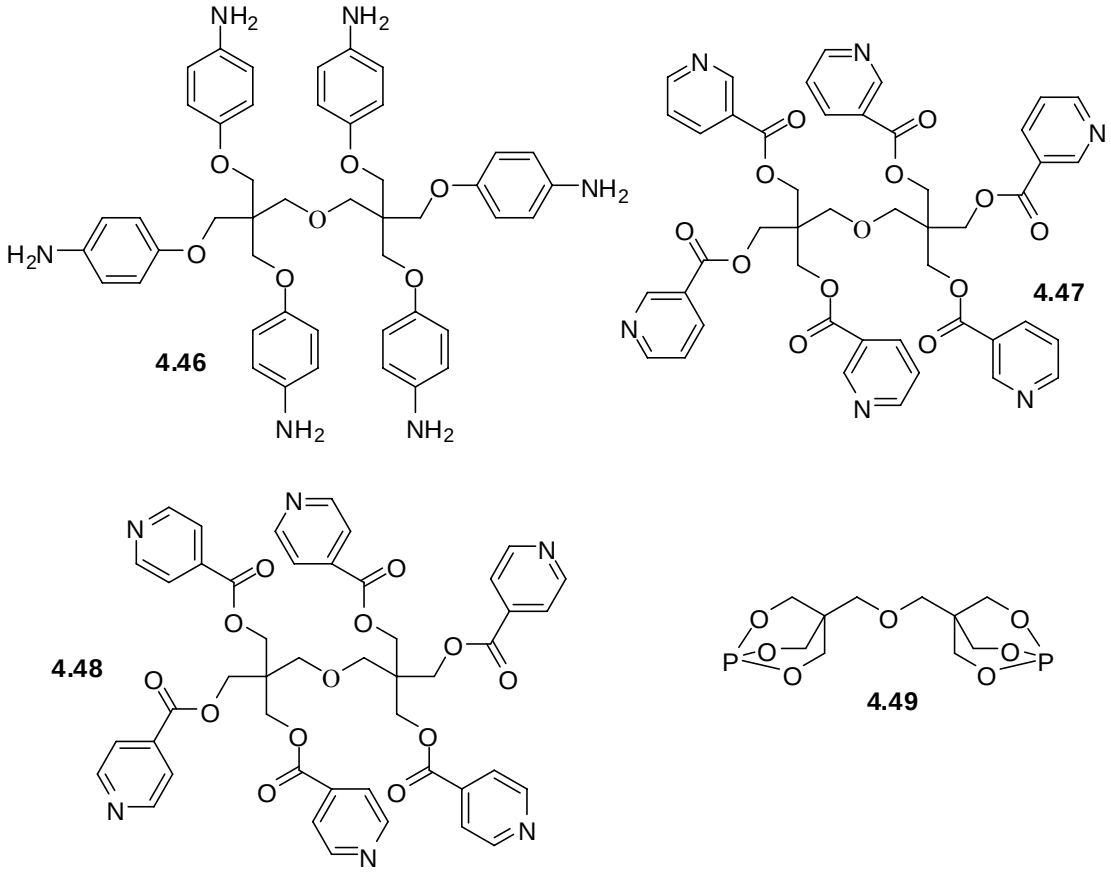
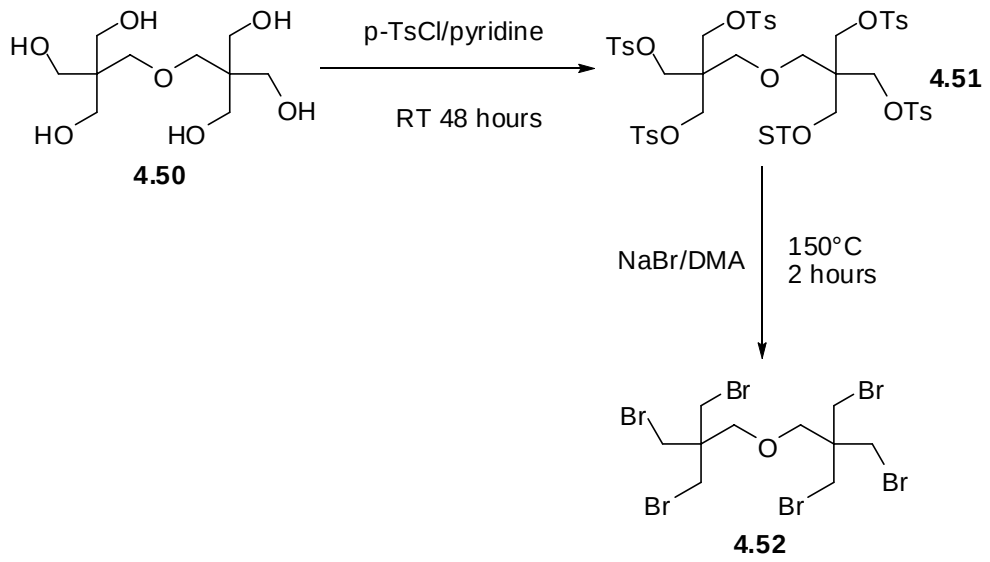


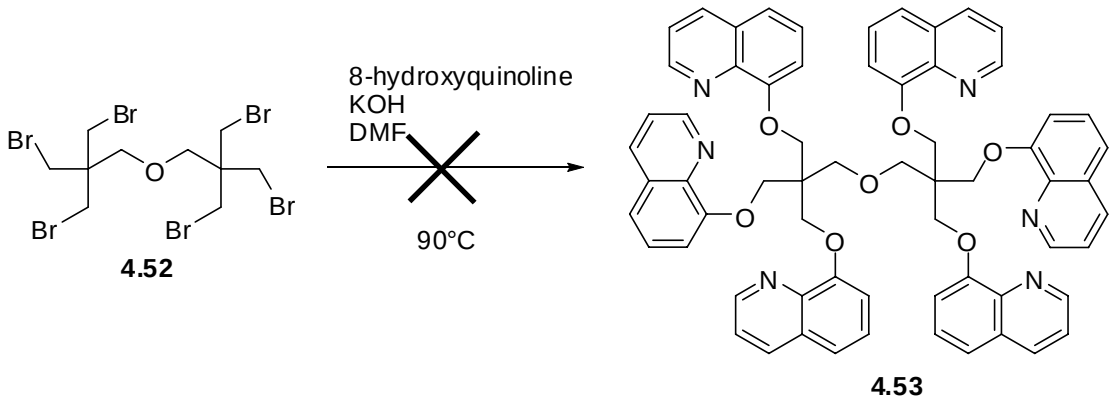
Figure 4.23 – *Examples of other dipentaerythritol based compounds in the literature.*

Hexasubstituted ligands designed around a dipentaerythritol core are exciting targets for organic synthesis. This is because as one increases the number of arms on the central core, one thereby increases the number of intermolecular interactions. The reaction scheme for DPE-Br6 (**4.52**), the precursor for the dipentaerythritol-based ligands, is shown in Scheme 4.10. DPE-Br6 was synthesised by the literature method of Shukla et al.,[260] which firstly involved converting the commercially available dipentaerythritol (**4.51**), 'DPE' for short, into the tosylate (**4.51**). The dipentaerythritol-based tosylate compound **4.51** was obtained in a good yield of 95%. The precursor **4.52** was then prepared by reaction of **4.51** with sodium bromide in dimethylacetamide in a reasonable yield of 53%. Precursor **4.52** was then reacted with various nitrogen heterocycles in order to generate a series of ligands.



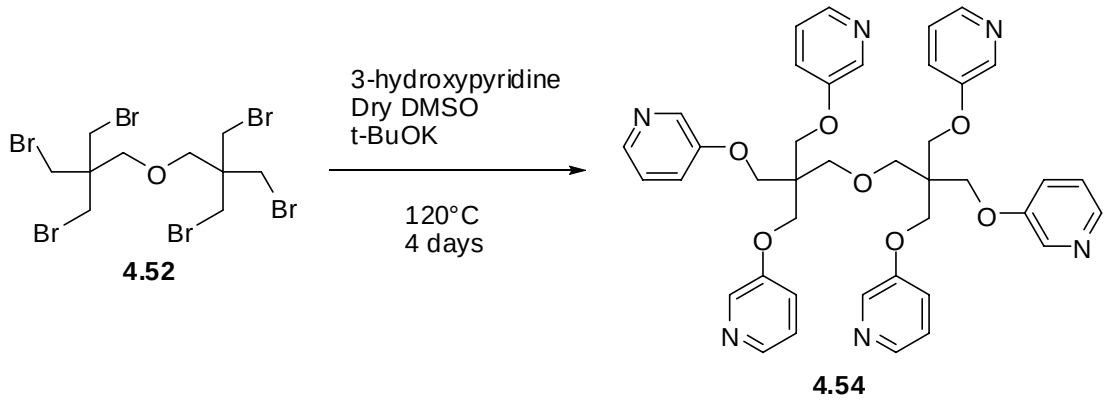
Scheme 4.10 – *Synthesis of ligand precursor DPE-Br6 (**4.52**).*

One of the target compounds, dipentaerythritol hexa(8-quinolyloxy)ether, **4.53**, is shown in Scheme 4.11. Attempts were made to synthesis ligand **4.53** using a similar method to that of Al-Mandhary and Steel via a base catalysed substitution reaction.[192, 255, 261-263] Unfortunately, the reaction did not occur as readily as expected and the desired product was not obtained after many days of reaction. Presumably this is because of the steric hinderance and over crowding caused by the addition of six quite bulky quinoline groups around the reasonably small dipentaerythritol core. It would seem that there would have to be some conformational adjustments to the ligand core in order to accommodate such large quinoline substituent groups. Several attempts were made to synthesise ligand **4.53** via this method, however it was not able to be isolated.



Scheme 4.11 – *Synthetic route to the dipentaerythritol-based ligand **4.53**.*

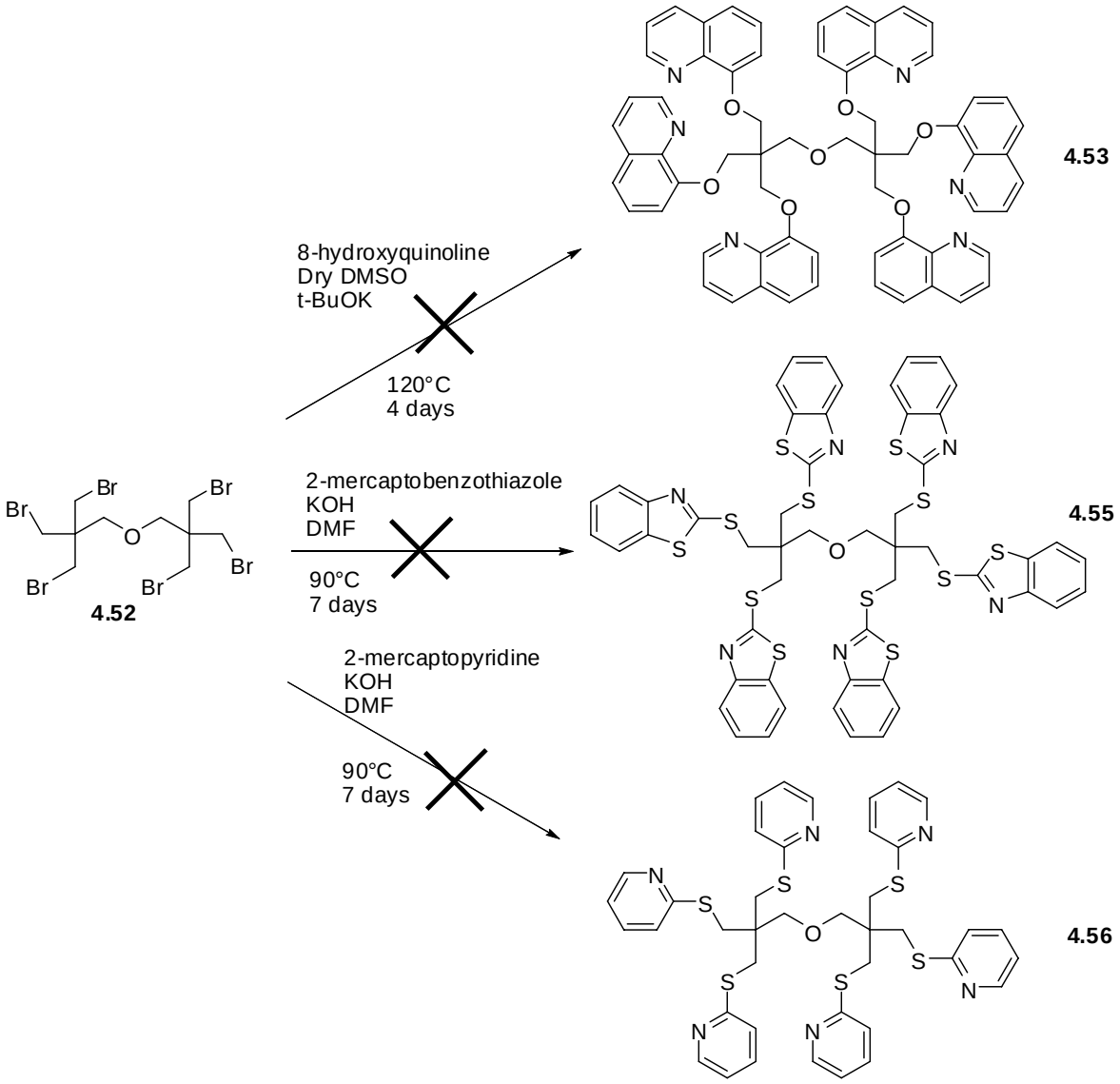
Previously Jana Vieth, a past member of the Steel group, synthesised the 3-pyridyl substituted dipentaerythritol ether based ligand, **4.54**,[264] as outlined in Scheme 4.12. Crystals of ligand **4.54** were grown and the X-ray structure was determined. This ligand **4.54** was synthesised via the same procedure, in a modest yield of 5.4%, after four days of reaction. The crude ligand **4.54** was recrystallised from a petroleum ether/ethyl acetate solution. Although, only a small amount of ligand **4.54** was obtained it was pleasing to have successfully made a hexasubstituted ligand. It is presumed that ligand **4.54** has less steric hinderance than ligand **4.53**, because the 3-pyridyl groups are considerably less bulky and can more easily arrange themselves around the central dipentaerythritol ether core. Ligand **4.54** was reacted with a variety of metal salts in the hope of constructing interesting metallosupramolecular species and/or arrays. Unfortunately, no complexes or subsequent crystal structures were obtained.



Scheme 4.12 – *Synthesis of ligand **4.54**.*

Due to the successful synthesis of ligand **4.54** by the base-catalysed reaction that substituted 3-hydroxypyridine groups onto the dipentaerythritol core, another attempt was made to synthesis the 8-hydroxyquinoline substituted ligand **4.53** under the same conditions. The second attempted synthesis of the quinoline substituted ligand **4.53** is shown in Scheme 4.13. After running the reaction for four days a crude brown solid was obtained in reasonable yield. Unfortunately, the ^{1}H NMR and mass spectrometry data proved to be ambiguous and seemed to suggest that the bulky 8-hydroxyquinoline groups had only reacted with two of the six dipentaerythritol arms. Presumably this is because the quinoline groups are bulky and therefore all six of the quinoline substituent groups are not able to attach to the dipentaerythritol core. As a consequence the

hexasubstituted ligand **4.53** was not isolated and no other synthetic routes to this ligand were attempted.



Scheme 4.13 – *Proposed synthesis of other hexasubstituted dipentaerythritol-based ligands.*

The syntheses of two more ligands based on the dipentaerythritol core are also outlined in Scheme 4.13. Ligands **4.55** and **4.56** were both synthesised via an analogous reaction to that shown in Scheme 4.11, in a method adopted by Al-Mandhary and Steel.[192, 255, 261, 262] The reaction involved the base-catalysed reaction substituting the bromine groups for 2-mercaptobenzothiazole or 2-mercaptopyridine groups. Both reactions were left running for seven days with continuous monitoring by ^{1}H NMR. Unfortunately the

hexasubstituted ligands **4.55** and **4.56** were not able to be isolated and no other synthetic routes to these ligands were attempted.

Summary

This chapter detailed the synthesis of various multi-substituted ligands. The first section discussed the synthesis and complexes of a new series of tripodal ligands based around a trisphenol substituted core, 1,1,1-tris(4-hydroxyphenyl)ethane. It is of great interest to study the coordination chemistry of tripodal ligands, because metallosupramolecular cage-like species are highly topical at the moment and tripodal ligands are amongst the most successful in constructing cage-like species. A total of seven tripodal ligands were synthesised and the X-ray structures of five of these were determined. The coordination chemistry of all seven ligands was studied. Although many complexes were made with the tripodal ligands with a large variety of metal salts only two crystal structures of complexes were obtained, one discrete and one polymeric.

A polymeric crystal structure was generated with the pyrazine substituted ligand **4.16** and CuI. The polymer had an interesting topology with only two of the ligand arms coordinating to copper metal centers, while the third arm lay pendent. However, the most fascinating complex synthesised was with ligand **4.15** and $CuCl_2$. X-ray analysis of the resulting crystals revealed a discrete M_3L_2 cage. This was very exciting, because one of the main reasons for synthesising the tripodal ligands was to attempt to generate molecular cages. The overall structure of the copper chloride M_3L_2 molecular cage was quite flat, as a result of the conformation of the ligand. Therefore, there was no central cavity within the cage and subsequently no encapsulation of any guest molecules.

No other crystal structures of complexes with the other tripodal trisphenol ligands were obtained, due to the low solubility of the corresponding complexes in most solvents. The low solubility of the ligands and their complexes could be due to the size and overall flexibility of the ligands.

Following on from this, attempts were made to synthesis various tetrasubstituted ligands. Ligands based around tetrakis(4-hydroxyphenyl)methane and 1,1,4,4-tetrakis(4-hydroxyphenyl)cyclohexane based cores were designed. Unfortunately, the

first step towards the synthesis of these ligand precursors was not successful and therefore no further reactions could be carried out.

A series of four-armed ligands based around a 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol based core was also synthesised. Five of these ligands were synthesised and the X-ray structures of two were determined. The coordination chemistry of these ligands was also investigated, but no crystal structures of any complexes were obtained.

Finally a new family of ligands was designed based on a dipentaerythritol core. There are few reports in the literature of such hexasubstituted ligands and no such reports of heterocyclic groups attached to a dipentaerythritol core. Therefore the coordination chemistry of these ligands could be interesting. Although the brominated ligand precursor **4.52** was able to be isolated in reasonable yield, the last steps involving the substitution of the heterocyclic groups onto the dipentaerythritol core were unsuccessful, despite numerous attempts. As a consequence the coordination chemistry of these hexasubstituted ligands was not studied.

Chapter Five

Bisphenol P and Bisphenol M based ligands

Chapter Five

Bisphenol P and Bisphenol M based ligands

Introduction

There have been many developments over the last decade in the field of metallosupramolecular chemistry. A great deal of this research involves the programmed self-assembly of metallosupramolecular species from the reaction of various bridging ligands with transition metal ions. Appropriate combinations of metal ions and bridging ligands lead to the controlled self-assembly of interesting and intricate one-, two- and three-dimensional molecular structures. Some of the simplest ligands to demonstrate this are bridging ligands that contain only two binding domains. These two binding domains can potentially link together two metal atoms to generate simple discrete molecular structures or polymeric assemblies. To date, one of the most commonly used bridging ligands are those that contain nitrogen containing heterocycles that are capable of bridging two metal atoms. Figure 5.1 shows some examples of simple nitrogen containing heterocyclic ligands that can coordinate up to two metal atoms to generate a wide variety of supramolecular topologies.[48, 265-269]

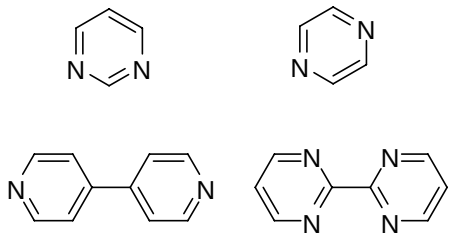


Figure 5.1 – *Some examples of nitrogen heterocyclic ligands that can coordinate to two metal atoms.*

One of the main aims in metallosupramolecular chemistry is to design ligands with specific properties so that these ligand building blocks can bind to metal centers in a desired fashion to create a particular structure. When designing a ligand one needs to consider a variety of contributing factors that may influence the ligand's ability to

coordinate to metal atoms and generate supramolecular arrays. Some of these factors include the geometry of the metal atom, coordination of anions, solubility in solvents, crystallisation and general reactivity. Thermodynamic and kinetic factors may also come into play, having a strong influence on potential products. Therefore, with all this in consideration, the overall ligand design is very important and can have a great deal of influence on the structure of the supramolecular array or species.[164] To date, a great deal of study has focused on the use of 'rigid' ligands as building blocks in supramolecular chemistry, in which the donor arms are locked into a particular position to generate a number of fascinating structures. A few examples of such 'rigid' ligands are shown in figure 5.1. On the other hand ligands of a more flexible nature can potentially form a larger range of structural topologies that the rigid ligand counterparts cannot achieve, due to their inherent flexibility. Ligands can be made more flexible by simply adding single atom spacer groups, such as ether oxygen atoms or methylene groups to the ligand core. The addition of extra spacer groups potentially allows the ligand itself to adopt quite different conformations with metal atoms in the solid state as a consequence of rotations around the single bonds.

The Steel group has been studying flexible ligands for some time now. In general, the flexible ligands are constructed from heterocyclic rings that are linked to aromatic groups via flexible spacer groups that are composed of combinations of methylene groups with sulfur or oxygen atoms. Figure 2.4 in chapter two shows a generalised picture of the ligands that have been made so far in the Steel group, as well as a detailed discussion of them. Most commonly a benzene ring has been used as the central scaffold between coordinating heterocyclic groups to generate many supramolecular complexes. However, one is not limited to having a benzene ring as the central scaffolding unit and numerous other arene cores have also been employed to bridge between heterocyclic units.

Ligands of a more flexible nature tend to lead to a larger number of different and fascinating structural topologies, such as helicates, rectangles and cages. Therefore it is advantageous to increase the size of a ligand by addition of extra flexible subunits. One of the simplest ways to increase the size of the ligand is to simply extend or attach more arms to the central core. The binding arms of the ligand will contain a heterocyclic group capable of coordinating to a metal center via a heteroatom or some other sort of

donor atom. In general, the ligand cores are aromatic, because this allows for a greater variety of substitutions around the ring and hence access to more ligands. However, one is not just limited to aromatic cores and a large variety of non-aromatic ligand cores have also been designed and synthesised. Two such examples of nitrogen heterocyclic ligands based around non-aromatic cores are illustrated in figure 5.2.[270, 271]

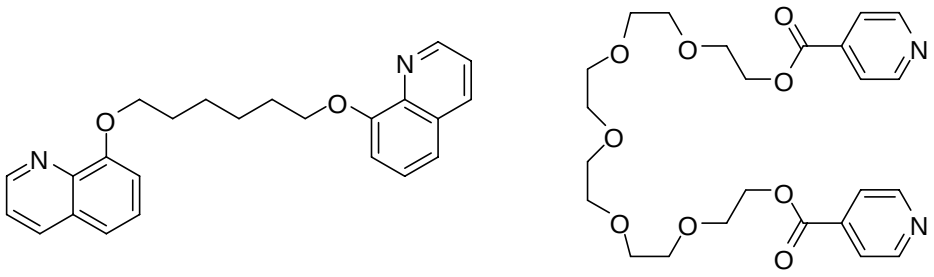


Figure 5.2 – *Two examples of nitrogen heterocyclic ligands based around non-aromatic ligand cores.*

Figure 5.3 illustrates some examples of nitrogen heterocyclic ligands based around aromatic cores other than just a single benzene that can bridge two metal atoms. The exploration of larger polycyclic aromatic cores allows multiple substitutions around the ring and more flexibility with the separation of donor arms around the central core. This is emphasised in the disubstitution of heterocyclic donor groups around a naphthalene ring in which there are ten possible isomers, as shown by O'Keefe.[118] Ligands **5.1** and **5.2** are examples of ligands with biphenyl as the central aromatic core unit. Recently, Fujita and co-workers have described the formation of some interesting complexes with ligand **5.1**. Treatment of ligand **5.1** with $Ni(NO_3)_2$ and $Cd(NO_3)_2$ generated large square grid-like polymers with cavities large enough to encapsulate guest molecules such as benzene or o-xylene molecules.[272-274] Subsequently they also described the formation of a unique tetrahedral complex with ligand **5.2** in which eight ligands are arranged around palladium metal atoms with two sides of the tetrahedron flanked by two ligands and the other four sides have only single ligand units.[275] Effectively this means that two of the edges of the tetrahedron are 'double-walled'. This is in contrast to other reported tetrahedral complexes in the literature that have only six ligands, one at each side of the tetrahedral framework. Ligand **5.1** can be extended by addition of another phenylene spacer group onto the ligand core to give ligand **5.3**. Complexation of ligand **5.3** with

$Ni(NO_3)_2$ produced a ladder network.[276] Insertion of this extra spacer unit allows the formation of even larger cavities than that of the square grid-like complexes formed with ligand **5.1**.

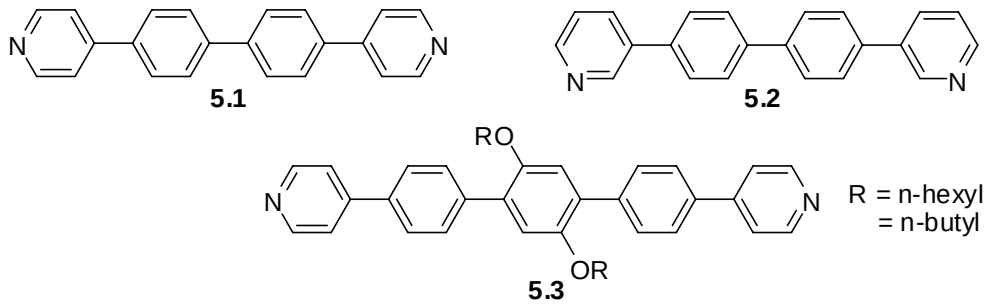


Figure 5.3 – *Examples of ligands based around aromatic cores capable of bridging two metal atoms.*

Figure 5.4 shows some examples of even larger nitrogen containing heterocyclic ligands based around aromatic cores that have been used over the years as synthons in metallosupramolecular chemistry. All of the ligands depicted in figure 5.4 have even more spacer units than that described above and this potentially allows for greater metal-metal separations in their metal complexes. This also allows for the formation of a more diverse range of metal complexes with less symmetrical topologies. This is emphasised by ligand **5.4**, which is made up of two 2,2'bipyridine units bound to a central biphenyl-3,3'-diyl spacer unit, and which forms a dinuclear double helicate with copper(I).[277] In 2002, McMorran et al. designed and synthesised the flexible multi-heterocyclic ligand **5.5**, which contained two different potential donor groups (pyrazine and pyridine) in the ligand structure.[135] Surprisingly, ligand **5.5** only coordinated to metal atoms through the nitrogens of the pyridine rings to generate large silver(I) and palladium(II) M_2L_2 macrocyles. Ligands need not be limited to just two binding domains and numerous ligands with multiple binding domains based around aromatic cores have also been successfully designed and synthesised over the years. Some examples of such ligands are ligands **5.6**-**5.8**, as shown in figure 5.4. Reaction of ligand **5.6** with $AgCF_3SO_3$ self-assembled into a spectacular 3 x 3 molecular grid composed of six ligand strands linked by nine silver atoms.[278] A few years later, Lehn and co-workers also reported the self-assembly of two quite different structures formed by the

combination of ligand **5.7** in the presence of other ligand molecules and copper(I) ions.[279] Finally, Lehn and co-workers reported the formation of a circular double helicate with ligand **5.8** and $FeCl_2$, whose internal cavity encapsulates a single chlorine ion.[280] Subsequent experiments found that the chlorine ion could not be exchanged for any other anions, therefore suggesting that the chlorine ion templates the self-assembly of the circular helicate.

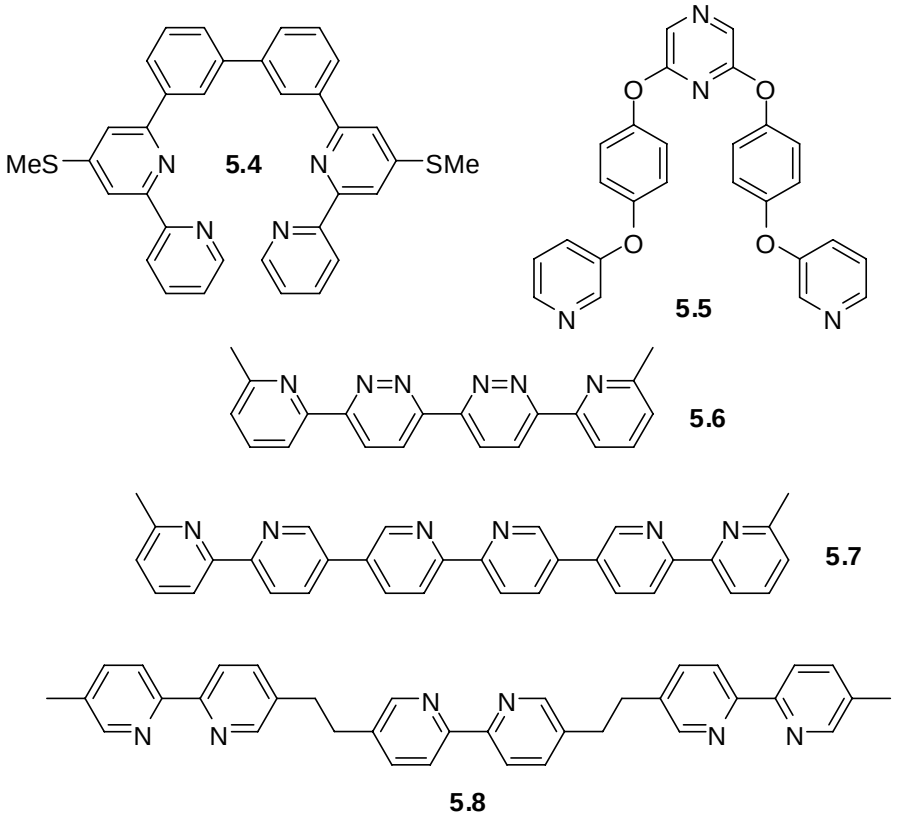


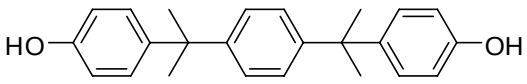
Figure 5.4 – *Examples of larger nitrogen containing heterocyclic ligands based around aromatic cores.*

This chapter describes the design and synthesis of a new range of bridging ligands based around more extended aromatic spacer units. The incorporation of spacer groups offers more flexibility with the orientation and substitution patterns of the heterocyclic donor groups, as well as larger inter-metallic separations between terminal nitrogen donor atoms. The larger distances between the nitrogen donor atoms will in turn control the separation of metal atoms in supramolecular complexes. The coordination chemistry of two armed bridging flexible ligands derived from Bisphenol A and Bisphenol Z backbones was explored in great detail in chapter two. This chapter will investigate the

synthesis of two new series of ligands based around Bisphenol M and Bisphenol P cores. These new bridging ligands are even more flexible than the Bisphenol A and Bisphenol Z derived ligands due to the incorporation of a propyl and phenylene spacer unit into the ligand structure. Bisphenol M and Bisphenol P were reacted with various haloazines and chloromethylpyridines to create a range of ligands capable of bridging two metal atoms. It is anticipated that the incorporation of the extra spacer groups into the ligand structure will lead to a number of different and fascinating supramolecular assemblies.

Synthesis of the Bisphenol P based -O- spaced ligands

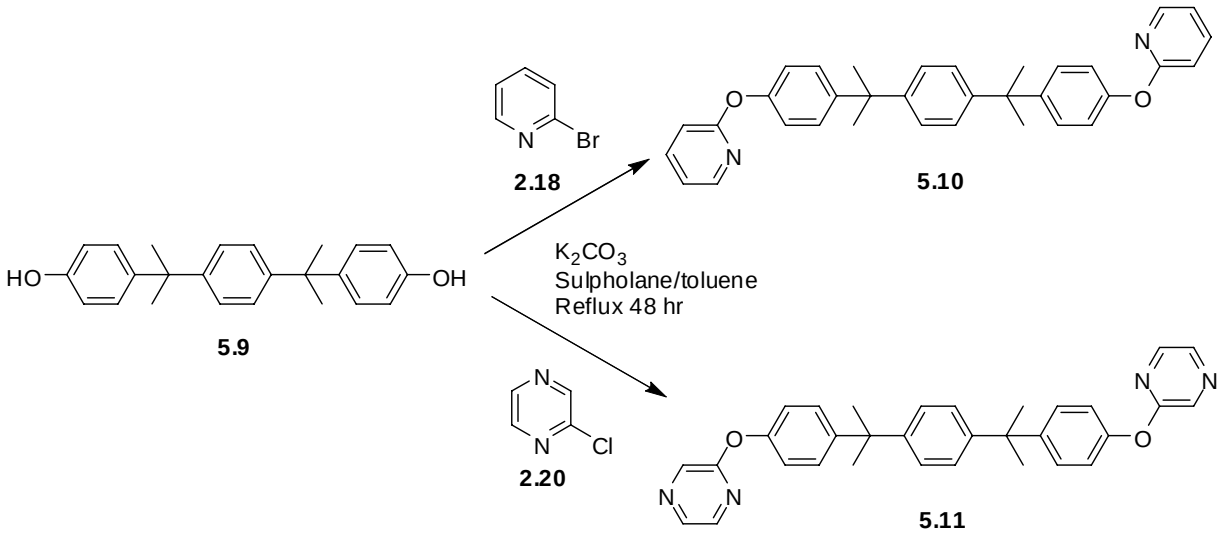
4,4'-(1,4-Phenylenediisopropylidene)bisphenol, commercially known as Bisphenol P, is essentially an extension of Bisphenol A by incorporation of an extra phenylene spacer group inserted between two propane groups and two benzene groups. The structure of Bisphenol P is shown in figure 5.5 below. The introduction of a phenylene and extra propyl spacer group into the ligand structure elongates the ligand structure and consequently increases the distance between nitrogen donor atoms of appended heterocycles.



5.9

Figure 5.5 – *Structure of Bisphenol P.*

The first two ligands synthesised from precursor **5.9** are shown in Scheme 5.1. New ligands **5.10** and **5.11** were synthesised by nucleophilic aromatic substitution of Bisphenol P with the haloazines 2-bromopyridine (**2.18**) and 2-chloropyrazine (**2.20**). This method is analogous to that of O'Keefe.[112] Recrystallisation of ligands **5.10** and **5.11** produced yellow and white solids in good yields of 100% and 69%, respectively.[113] Subsequently, these ligands were fully characterised and crystals suitable for X-ray crystallography were grown of the pyridine substituted ligand **5.10**.



Scheme 5.1 – *Synthesis of ligands **5.10** and **5.11**.*

Crystal structure of ligand 1,4-di((2-4-(2-pyridyloxy)phenyl)prop-2-yl)benzene, 5.10

Colourless crystals of ligand **5.10** were grown from a mixed solution of ligand **5.10** and zinc bromide. Ligand **5.10** crystallises in the monoclinic space group C2/c with half a molecule in the asymmetric unit, with a crystallographically imposed centre of inversion positioned at the centroid of the central phenyl ring. The crystal structure of ligand **5.10** is shown in figure 5.6, with the hydrogen atoms omitted for clarity. The addition of a phenylene spacer group enables the ligand to adopt a zig-zag conformation, which is clearly seen in figure 5.6. The pyridine rings of the ligand are facing in opposite directions away from one another and are almost perpendicular to the attached benzene rings and each of the nitrogen atoms is pointing inwards towards the centre of the attached pyridine ring with a low N-C-O-C torsional angle of 8.3°. The introduction of the extra spacer group increases the distance between nitrogen atoms to 16.810Å. This is quite significant in comparison to the distances observed between potential donor atoms in the smaller Bisphenol A and Bisphenol Z ligands.

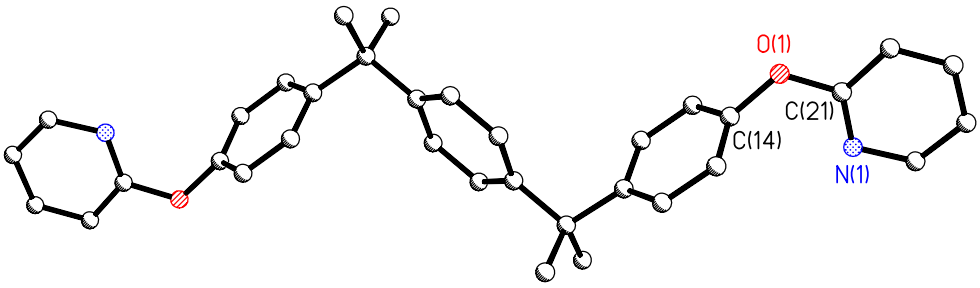
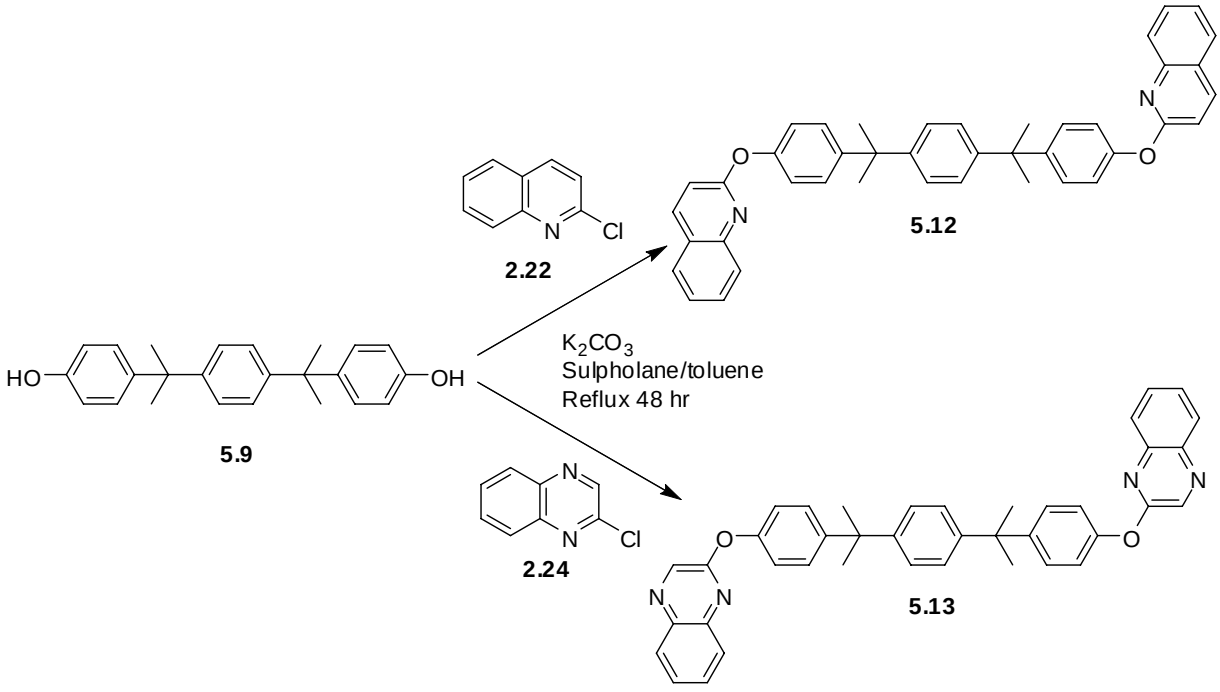


Figure 5.6 – *Crystal structure of ligand **5.10**, with the hydrogens omitted for clarity. Selected bond lengths (Å) and angles (°): C14-O1 1.400(3), O1-C21 1.354(3), C21-N1 1.312(3), C21-O1-C14 120.1(2), N1-C21-O1 118.9(2).*

The next two ligands synthesised from ligand precursor **5.9** are outlined in Scheme 5.2. New ligands **5.12** and **5.13** were synthesised by an analogous reaction to that shown in Scheme 5.1 with the larger haloazine heterocycles 2-chloroquinoline (**2.22**) and 2-chloroquinoxaline (**2.24**). Crude ligands **5.12** and **5.13** were subsequently recrystallised to produce white and yellow solids in yields of 87% and 39%, respectively.[112, 113] Subsequently, these ligands were fully characterised and crystals suitable for X-ray crystallography were grown of the quinoline substituted ligand **5.12**.



Scheme 5.2 - *Synthesis of ligands **5.12** and **5.13**.*

Crystal structure of ligand 1,4-di((2-4-(2-quinolyloxy)phenyl)prop-2-yl)benzene, 5.12

Crystals of ligand **5.12** were grown from a mixed solution of ligand **5.12** and copper nitrate. It was of no surprise that the crystals turned out to be just the ligand, because the crystals were colourless. The ligand crystallises in the monoclinic space group $P2_1/c$ with half a ligand molecule in the asymmetric unit and no solvent molecules. The crystal structure of the full ligand **5.12** is shown in figure 5.7, with the hydrogen atoms omitted for clarity. The ligand molecule has a centre of inversion positioned at the centroid of the central benzene ring. Once again, the addition of a phenylene spacer group allows the ligand to adopt a zig-zag type conformation similar to that seen in ligand **5.10** described above. The only point of difference between the zig-zag patterns of the two ligands is the overall conformation. The conformation of ligand **5.10** is composed of 'V'-shaped zig-zag units, whereas ligand **5.12** has two 'U'-shaped zig-zag patterns. This is more clearly seen in the space-filling diagram of ligand **5.12** shown in figure 5.8. Overall ligand **5.12** adopts an S-shaped conformation. The nitrogen atoms of the quinoline heterocycle groups are twisted to point inwards towards the centre of the ligand structure to face the central phenylene spacer group, which is reflected in the low N-C-O-C torsional angle of 3.6°. The orientation of the nitrogen atoms to point inwards on ligand **5.12** means the two quinoline groups will have to twist around in order to bind to metals. The separation between nitrogen donor atoms in ligand **5.12** is 14.893Å, which is slightly less than the distance between nitrogen donor atoms in ligand **5.10**. In the crystal packing there are few significant interactions between ligand molecules.

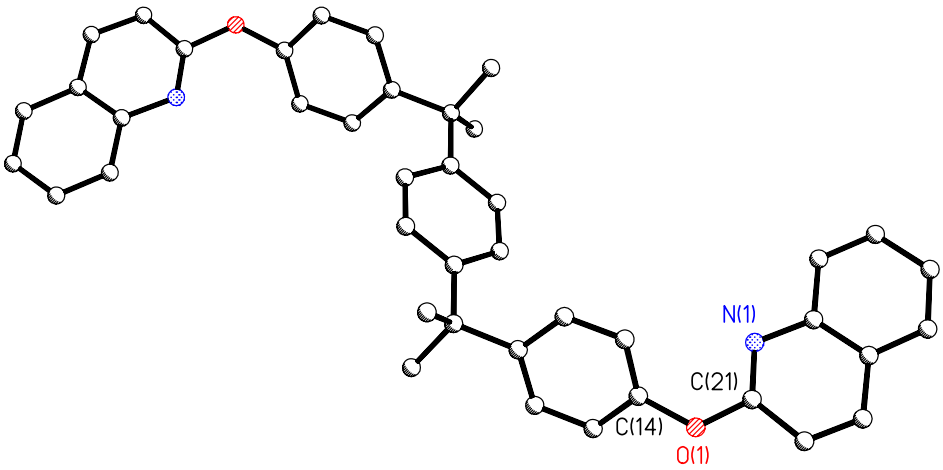


Figure 5.7 - *Crystal structure of ligand* ***5.12****, with the hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): C14-O1 1.400(2), O1-C21 1.364(2), C21-N1 1.297(2), C21-O1-C14 123.8(1), N1-C21-O1 121.5(2).*

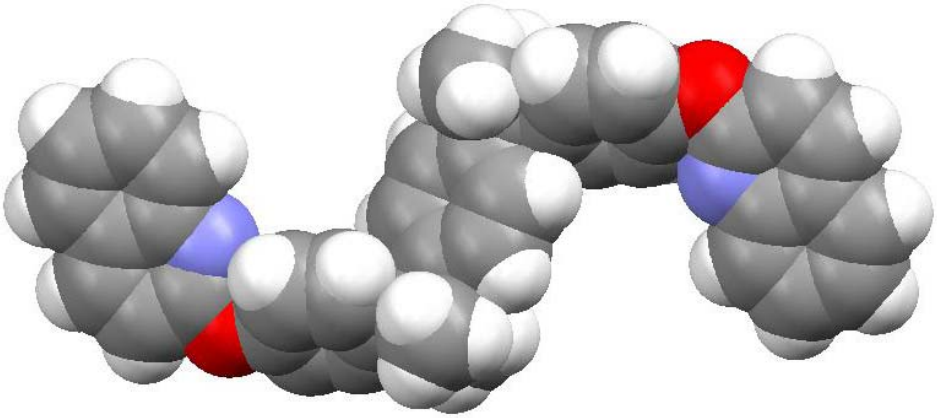


Figure 5.8 – *Space-filling diagram of ligand* ***5.12****. If one rotates this diagram by 90° in either direction it looks like an S-shaped component.*

There are few reports in the literature of ligands having Bisphenol P derived backbones. Therefore, it is logical to focus a research project on ligands based around a Bisphenol P backbone. However, a literature review did reveal a few intriguing compounds incorporating Bisphenol P units that have been synthesised and investigated in the literature over the last ten years. Recently, Bartsch et al. synthesised a new range of

cyclophane host molecules constructed from two Bisphenol P units linked through the phenolic oxygens that are bridged by two multi-methylene spacer groups, as shown in figure 5.9.[281] These bisphenol units gave open structures with central cavities that could be made larger by simply altering the number of carbon atoms in the alkylidene spacer groups. The cyclophane host molecules contained hydrophobic cavities and therefore Bartsch et al. envisaged the formation of complexes by insertion of aromatic guest molecules inside the cavity of the host. This type of cyclophane host is called a 'corral' host. In fact, Bartsch et al. reported a couple of crystal structures of corral host molecules with aromatic guest molecules such as *p*-xylene and anthracene inside the host cavity.[282] The complex formed with anthracene and the corral host bridged by five carbon atoms in the spacer groups exhibited edge-to-face interactions between guest and host molecules.

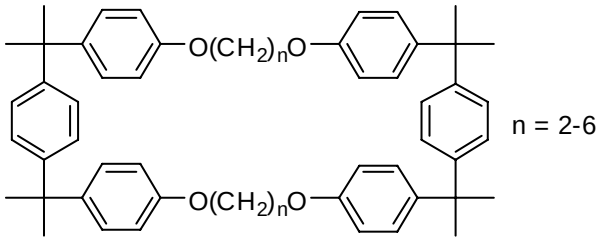


Figure 5.9 – *Illustration of cyclophane host molecules containing Bisphenol P units synthesised by Bartsch et al.*

Previously, in 1996, Bartsch et al. generated a series of ferrocenophanes derived from Bisphenol P that contained hydrophobic pockets envisaged to encapsulate neutral molecules.[283] An X-ray structure was obtained of one of the ferrocenophanes that revealed a small central cavity. Unfortunately, the cavity was found to be too small to encapsulate any guest molecules.

Bauer et al. designed and investigated fascinating isomeric phosphite caged cryptand molecules derived from Bisphenol P and PCl_3, as illustrated in figure 5.10.[284] Caged compounds are currently a hot topic in the field of supramolecular chemistry. Astoundingly, the isomeric caged molecules were the preferred product from the one-pot tri-capping method synthesis, which was a surprise to them because one would not

expect this due to the flexible arms of Bisphenol P. The isomers were subsequently separated by column chromatography and X-ray structures of the macrobicycles **1** and **2** were obtained and analysed. The X-ray structures revealed no C_3 symmetry in the P-P direction as they had expected. Following on from this Bauer et al. carried out further studies on the phosphite caged compounds by reacting them with thiophosphoryl azide to effectively introduce other groups into the cavity.[285]

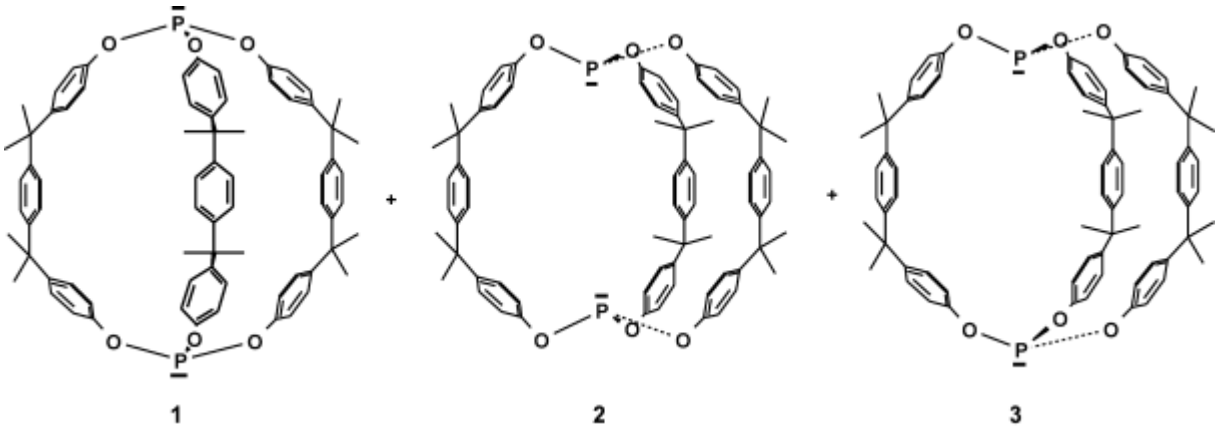


Figure 5.10 – *The three isomeric phosphite caged cryptand molecules derived from Bisphenol P and PCl_3.*

The literature review revealed only a few compounds based around a Bisphenol P core. Therefore, it was logical to design a range of new ligands based around a Bisphenol P core and from these make complexes and produce crystals suitable for X-ray analysis.

Complexes with ligand 5.10

*Crystal structure of the complex with $CoBr_2$ (**5.14**)*

Slow evaporation of an acetone solution of ligand **5.10** and cobalt bromide produced clumps of blue crystals suitable for X-ray crystallography after four days. Analysis of the crystals revealed a one-dimensional zig-zag coordination polymer. Complex **5.14** crystallises in the monoclinic space group C2/c with half a ligand molecule, half a cobalt, one bromine atom, an acetone molecule and an acetonitrile molecule in the asymmetric unit. A section of the one-dimensional polymeric structure is shown in figure 5.11, which is grown to show the connectivity around the cobalt metal atoms in

the extended structure. The hydrogens and disordered solvent molecules have been omitted for clarity.

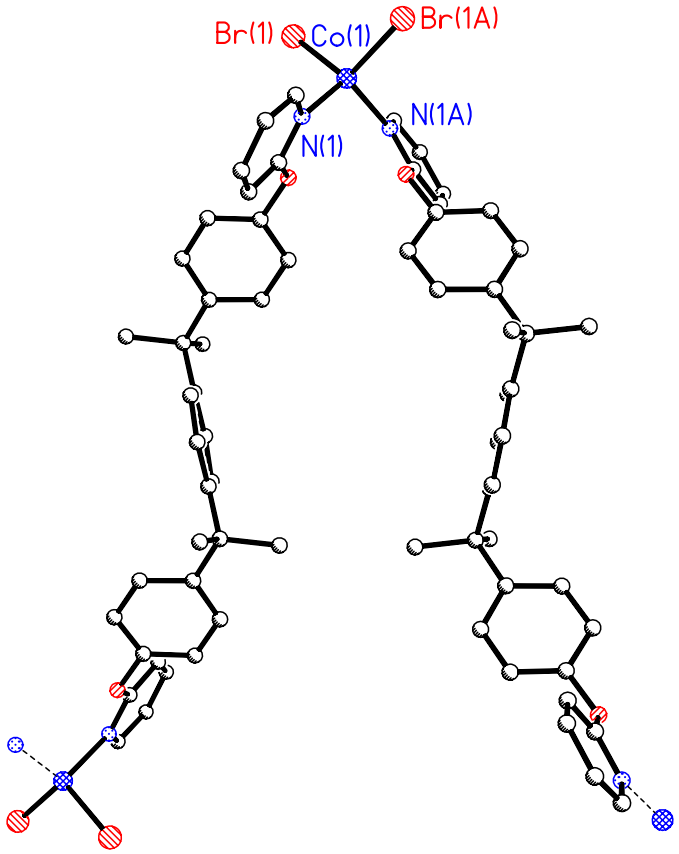


Figure 5.11 – *A small section of the cobalt bromide one-dimensional polymer* ***5.14****. Selected bond lengths (Å) and angles (°): Co1-N1 2.044(2), Co1-Br1 2.3780(4), N1-Co1-N1A 112.8(1), N1-Co1-Br1A 104.46(6), N1-Co1-Br1 110.94(6), N1A-Co1-Br1A 110.94(6), N1A-Co1-Br1 104.46(6), Br1-Co1-Br1A 113.50(2).*

In complex **5.14**, the cobalt atom is coordinated to two pyridine nitrogen atoms and two bromine atoms with a distorted tetrahedral geometry. The cobalt atom lies on a two-fold rotation axis and links together two ligands while each ligand is bridging two cobalt metal atoms. In complex **5.14,** the ligand adopts a zig-zag conformation of its own. The pyridine rings of each ligand are facing in opposite directions away from one another and are almost perpendicular to the attached benzene rings. In fact, the conformation of the ligand in complex **5.14** is remarkably similar to that of the free ligand **5.10** in the solid state. The Co-N bond length is 2.044Å and the Co-Br bond length is 2.378Å, both of which are similar to other cobalt bromide complexes described so far in this thesis.

The polymer propagates in one-dimension in a zig-zag pattern, with the cobalt atoms acting as the corner pivots of the zig-zag pattern linking together the jagged ligand strands. The zig-zag formation of complex **5.14** is very symmetrical and is more clearly seen in a larger section of the polymer as depicted in figure 5.12, with the hydrogens and solvent molecules omitted for clarity. As illustrated in figure 5.12 each of the ligands bridges together two cobalt atoms and each of the cobalt atoms is coordinated to two bromine atoms and two pyridine nitrogen atoms. The ligand strands are jagged due to the conformation of the ligand in the complex and the overall zig-zag conformation of the ligand itself. The nearest distance between cobalt atoms in the chain is 16.801Å, which is the distance traversed between two cobalt atoms and two ligand strands along the zig-zag chain. The distance between two cobalt atoms bridged by a single ligand molecule is 20.336Å.

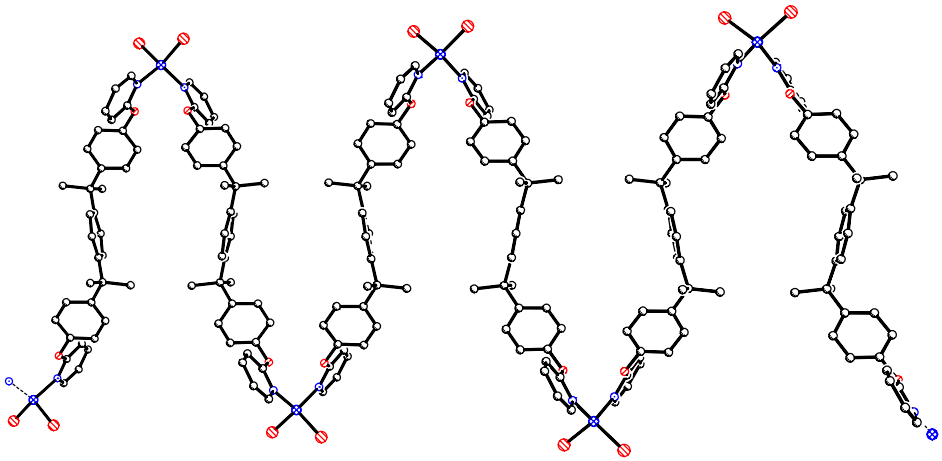


Figure 5.12 – *View of the one-dimensional zig-zag polymer* ***5.14***.

In the packing the zig-zag chains align with only edge-to-face interactions between benzene rings and pyridine rings (2.500Å) of adjacent strands. There are no other interactions observed between ligands in the extended structure. However, there are some hydrogen bonding interactions between solvent molecules and the polymeric strands.

*Crystal structure of the complex with $CoCl_2$ (**5.15**)*

After a couple of days of slow evaporation, clusters of star-like crystals grew from an acetone solution of ligand **5.10** and cobalt chloride. The star-like crystal clusters were able to be broken apart to give smaller blue crystals that were air stable and consequently suitable for X-ray crystallography. However, all the crystals that were put up on the X-ray diffractometer gave poor diffraction patterns that were also indicative of the crystal being twinned. Several attempts were made to re-grow and recrystallise the complex under different conditions; however only one X-ray structure could be obtained, which was of poor quality. The best dataset obtained resulted in a large R_1 value of 18.30%. The crystal structure solved in the triclinic space group P-1. Interestingly, the asymmetric unit contains four independent half-ligands, two cobalt atoms and four chlorine atoms. The asymmetric unit also contains a whole acetone molecule. There are two independent units in the asymmetric unit that each grow into separate one-dimensional polymer strands.

Although the two ligand/cobalt strands are similar, they are not identical. In complex **5.15** both of the ligands adopt a similar conformation to that seen in the crystal structure of ligand **5.10** itself. The same zig-zag conformation is generated in each of the ligand strands in complex **5.15** as a consequence of the central phenylene spacer group. The pyridine binding arms of both ligands are also oriented to face in opposite directions away from one another in order to coordinate to the cobalt metal atoms and once again the pyridine rings are almost perpendicular to the attached benzene rings in both ligands. Therefore, the conformations of both ligands strands are almost identical. The main difference between the two ligand strands is seen in the orientation of the pyridine ring to the attached benzene ring. In the ligand strand attached to Co1 the pyridine rings are almost perpendicular to the attached benzene rings, which is reflected in the angles between the planes of the two rings of 89.5° and 57.4°. On the other hand the ligand strand attached to Co2 has the pyridine rings less orthogonal to the attached benzene rings and more tilted away from the plane of the attached benzene ring with angles of 78.3° and 55.7°.

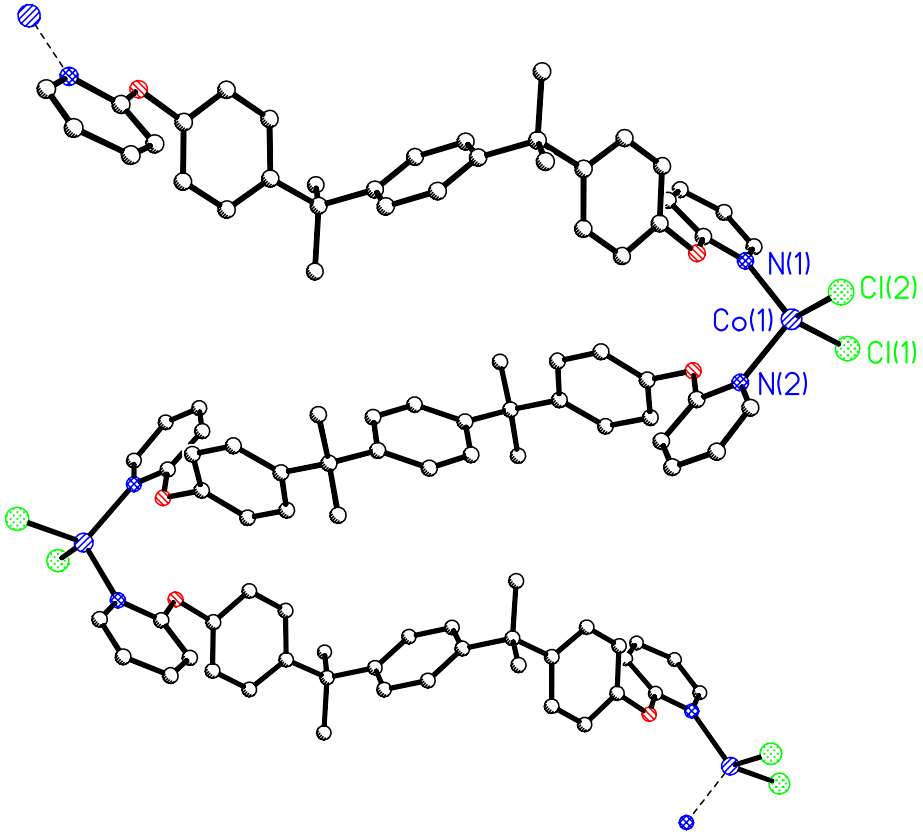


Figure 5.13 – *A section of the polymer strand attached to Co1 metal atom in complex* ***5.15****. Selected bond lengths (Å) and angles (°): Co1-N1 2.050(1), Co1 N2 2.065(1), Cl1-Co1 2.228(4), Cl2-Co1 2.235(3), N1-Co1-N2 109.9(4), N1-Co1-Cl1 104.1(3), N2-Co1-Cl1 111.2(3), N1-Co1-Cl2 116.9(3), N2-Co1-Cl2 104.3(3), Cl1-Co1-Cl2 110.6(2).*

The two ligand/cobalt units in the asymmetric unit each grow into separate one-dimensional polymer strands. A section of the one-dimensional polymer of the ligand/cobalt strand attached to the Co1 metal atom is shown in figure 5.13, with the hydrogens and acetone solvent molecule omitted for clarity. In the Co1 polymer strand the coordination geometry of cobalt is distorted tetrahedral with the largest deviation from tetrahedral being 116.9°. The four-coordinate cobalt atom is coordinated to two pyridine nitrogen atoms and two chlorine atoms. Each cobalt atom links together two ligands and each ligand bridges two cobalt metal atoms. The overall result is a one-dimensional zig-zag polymer similar in topology to the cobalt bromide complex **5.14** described above. The polymer has cobalt atoms acting as the corners of the overall zig-zag pattern linking together jagged ligand strands. The distance between closest cobalt

atoms in the zig-zag chain is 17.308Å, which is slightly larger than the corresponding distance in complex **5.14**.

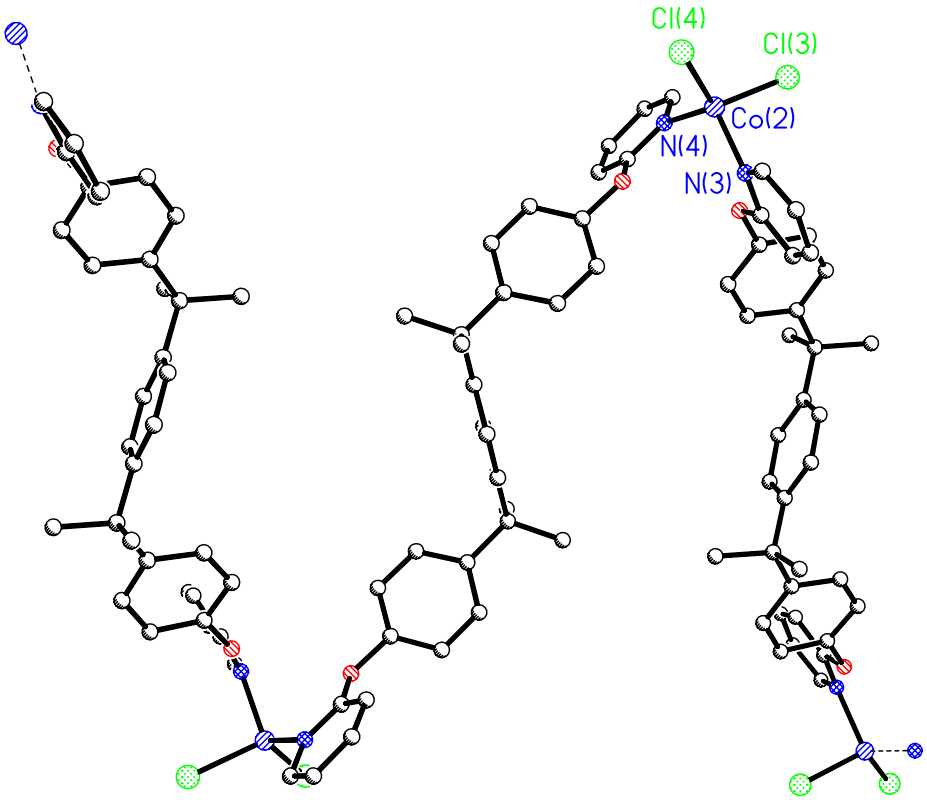


Figure 5.14 - *A section of the polymer strand attached to Co2 metal atom in complex* ***5.15****. Selected bond lengths (Å) and angles (°): Co2-N3 2.046(1), Co2-N4 2.035(1), Co2-Cl3 2.241(4), Co2-Cl4 2.222(4), N4-Co2-N3 116.1(4), N4-Co2-Cl4 114.9(3), N3-Co2-Cl4 106.0(3), N4-Co2-Cl3 103.8(3), N3-Co2-Cl3 99.9(3), Cl4-Co2-Cl3 115.6(2).*

A section of the one-dimensional polymer of the ligand/cobalt strand attached to the Co2 metal atom is shown in figure 5.14, with the hydrogens and acetone solvent molecule omitted for clarity. As stated before and seen in the two figures, the two cobalt polymer chains are almost identical to each other having the same zig-zag topology. In the Co2 polymer strand the coordination geometry of the cobalt atom is also distorted tetrahedral with an even larger deviation from tetrahedral of 99.9°. The cobalt atom is also bound to two pyridine nitrogen atoms and two chlorine atoms so that each ligand is bridged by two cobalt metal atoms. The ligand molecules in the Co2 strand have the same jagged zig-zag topology and the bond lengths and bond angles are also similar to those seen in the Co1 polymer strand. The distance between adjacent cobalt atoms in

the Co2 chain is 17.502Å, which is also within the range of the distance between adjacent cobalt atoms in the Co1 polymer chain.

In the crystal packing the acetone molecules interact through various hydrogen bonding interactions with the two one-dimensional cobalt polymer strands. There are also hydrogen bonding and C-H···Cl interactions between the ligand molecules of separate cobalt strands.

*Other complexes with ligand **5.10***

The Bisphenol P derived ligand **5.10** was reacted with a variety of metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $Pd(PhCN)_2Cl_2$, $ZnCl_2$ and $ZnBr_2$. Crystals suitable for X-ray analysis were obtained with both of the cobalt metal salts resulting in two similar one-dimensional zig-zag polymers. Unfortunately, crystals suitable for X-ray analysis were not able to be grown upon complexation with any other metal salts. Some of the complexes with ligand **5.10** gave immediate precipitates, whereas others formed precipitates upon slow evaporation. Some of these precipitates were subsequently analysed by elemental analysis and are described below. Sometimes crystals of just the ligand **5.10** itself were grown from the mixed solution.

Complexation of ligand **5.10** with $CuCl_2$ gave a fine green precipitate on standing for a few days that analysed with a 2:1 ratio of metal to ligand. This stoichiometry suggests some sort of polymeric structure composed of ligands linked together by Cu_2Cl_4 square motifs. Such copper chloride square motifs are not uncommon and have been explored a few times so far in this thesis with the Bisphenol A and Bisphenol Z derived ligands.

Slow evaporation of a solution containing $Cu(ClO_4)_2$ and ligand **5.10** produced a blue solid that analysed with a ML_2 stoichiometry. This 1:2 ratio of metal to ligand suggests the possible formation of a discrete complex or perhaps a polymeric complex.

Reaction of $PdCl_2$ with ligand **5.10** gave a yellow precipitate immediately. Elemental analysis revealed a 1:1 ratio suggesting the formation of a polymer or a simpler discrete complex.

The last complex to be analysed by elemental analysis was the yellow precipitate formed upon complexation with $Pd(PhCN)_2Cl_2$, which analysed with a M_2L stoichiometry just like the $CuCl_2$ complex. Ligand **5.10** can only coordinate to two metal atoms; therefore this stoichiometry suggests the formation of a discrete complex. The alternative is a polymer made up of ligands that are linked together via palladium squares, similar to that of the copper chloride square motifs.

Complex with ligand 5.11

*Crystal structure of the complex with $CuCl_2$ (**5.16**)*

Slow evaporation of a solution containing the pyrazine substituted ligand **5.11** and copper chloride furnished green plate-like crystals suitable for X-ray crystallography. Unfortunately, the crystals were air sensitive and decomposed rapidly after removal from solvent, cracking after only a few minutes even when stored in oil. Therefore it took a few attempts to finally mount a suitable crystal onto the diffractometer as fast as possible without losing crystallinity. All of the crystals that were put up on the diffractometer diffracted weakly and gave poor diffraction patterns that were indicative of the crystal being twinned. Despite this, eventually a dataset was collected that provided a poorly refined structure with a large R_1 value of 18.11%. Unfortunately, the data were only adequate enough to refine the coppers and chlorides anisotropically. All of the other atoms were only able to be refined isotropically. Several attempts were made to re-grow and/or recrystallise the crystals to obtain better quality crystals; however this still remains the best and only dataset for this structure. The complex crystallises in the triclinic space group P-1 with one and a half ligands, one and a half copper atoms and three chlorine atoms in the asymmetric unit, as shown in figure 5.15. The complex grows into an intricate complex composed of three ligand strands that are linked by Cu_3Cl_6 bridged motifs into a two-dimensional sheet.

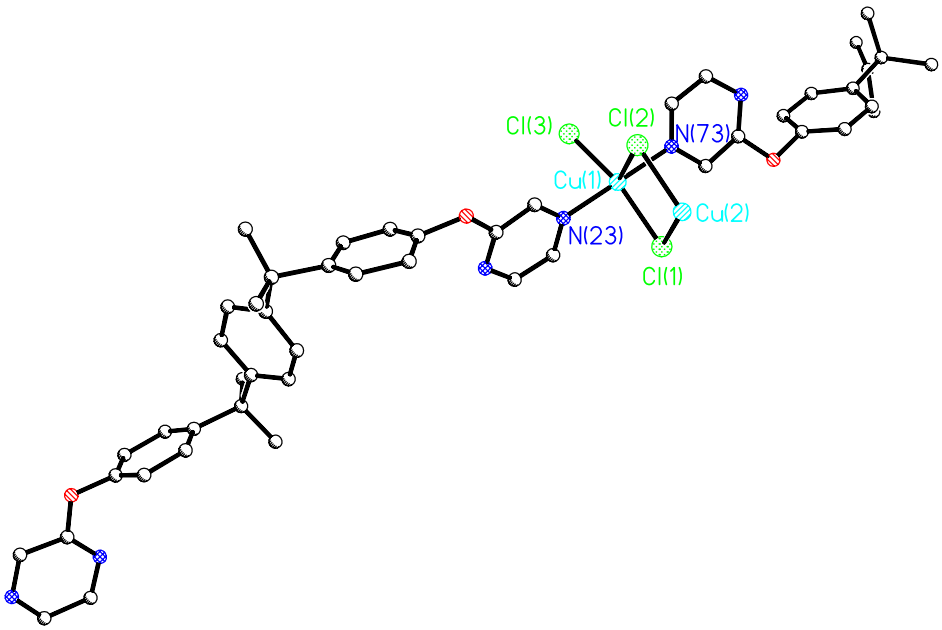


Figure 5.15 – *Perspective view of the contents of the asymmetric unit of complex* ***5.16****. Selected bond lengths (Å) and angles (°): Cu1-N73 2.031(2), Cu1-N23 2.027(2), Cu1-Cl3 2.263(1), Cu1-Cl1 2.353(6), Cu1-Cl2 2.615(7), Cu2-Cl2 2.354(6), Cu2-Cl1 2.751(6), N73 Cu1 N23 179.9(8), N73-Cu1-Cl3 92.5(5), N23-Cu1-Cl3 87.6(5), N73-Cu1-Cl1 92.6(5), N23-Cu1-Cl1 87.3(5), Cl3-Cu1-Cl1 162.9(4), N73-Cu1-Cl2 84.5(4), N23-Cu1-Cl2 95.6(5), Cl3-Cu1-Cl2 104.2(4), Cl1-Cu1-Cl2 92.6(2), Cu2-Cl2-Cu1 90.7(2), Cu1-Cl1-Cu2 87.4(2),*

In the complex there are two independent copper(II) atoms, with quite different coordination geometries. The Cu2 atom lies on a crystallographic centre of inversion. Each of the copper(II) atoms is coordinated to two pyrazine nitrogen atoms from separate ligand strands and subsequently linked by di(μ-chloro) bridges. The overall result is a trimeric copper chloride motif composed of three copper(II) atoms that are bridged by two di(μ-chloro) bridges. An illustration of the trimeric copper chloride bridging unit is depicted in figure 5.16 showing the two different coordination environments of the copper atoms. The central Cu2 atom that lies on a crystallographic centre of inversion has a pseudo-octahedral geometry binding to two pyrazine nitrogen atoms and four bridging chlorine atoms. As expected the copper atom coordinates to the ligand through the less hindered nitrogen atom of the pyrazine binding group. The basal plane is occupied by the four bridging chlorine atoms and the apical positions are occupied by the nitrogen atoms of the ligands. Consequently, the two nitrogens from the ligands are *trans* with respect to each other with a bond length of 2.050Å. The Cu2

bridges to the chlorine atoms with bond distances of 2.354Å and 2.751Å. These Cu-Cl bond lengths are well within the range observed in other di(μ-chloro)copper(II) complexes.[286] The other copper atom (Cu1) has a distorted square-pyramidal geometry and binds to two nitrogen atoms from separate ligands, two bridging chlorine atoms (Cl1 and Cl2) that link to Cu2 and one monodentate chlorine atom (Cl3). The two chlorine atoms and two pyrazine nitrogen atoms form the N_2Cl_2 basal plane and the apical position is occupied by one of the bridging chlorine atoms. The Cu-N bond lengths about Cu1 are 2.027Å and 2.031Å and the Cu-Cl bond lengths are 2.353Å and 2.263Å. The bridging chlorine atom in the apical position has a much longer bond length of 2.615Å, as a consequence of Jahn-Teller distortion. Although this Cu-Cl bond is longer than any others surrounding the Cu1 center, it is slightly shorter than the axially elongated Cu-Cl bond in the octahedral coordination sphere of Cu2. The unique copper(II) chloride motif looks symmetrical but is actually asymmetrical as reflected by the bond lengths and angles around the copper centers. The copper atoms are separated by a distance of 3.539Å between the asymmetric chloride bridges, which is about average for such di(μ-chloro)copper(II) complexes.

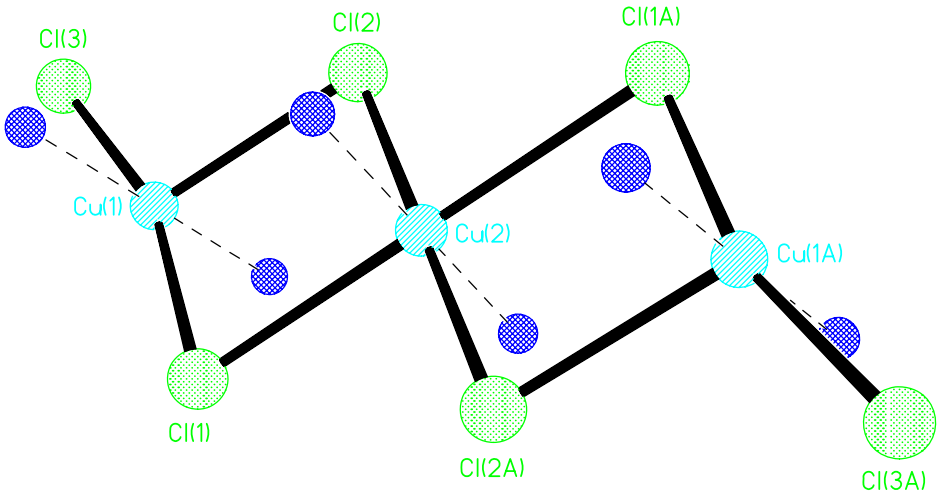


Figure 5.16 – *An illustration of the trimeric copper(II) bridging motif illustrating the coordination environments of the two different copper(II) centers.*

Each of the copper chloride motifs coordinates to six different ligands through the least hindered nitrogen atom of the pyrazine ring. Each ligand therefore coordinates to two separate copper chloride units. Overall the resulting complex is a two-dimensional

polymer that extends into a complex two-dimensional sheet. A perspective view of the two-dimensional sheet is shown in figure 5.17. A larger section of the same sheet is shown in figure 5.18. If one follows the ligand strands from one trimeric copper chloride bridging motif, two of the ligand strands link to the same copper chloride bridging unit, while the other ligand links to another copper chloride unit directly above this. The same coordination pattern occurs on the other side of the copper chloride bridging motif, which is all a result of the inversion centre that lies on the Cu2 metal centre. The two-dimensional sheet has quite large cavities as a result of the overall topology, unfortunately these cavities do not appear to play host to any guest molecules. The large cavities create square shaped voids in the sheet that have a diameter of approximately 18.118Å, which is the distance between the terminal Cu1 atoms of the copper chloride bridging units that lie directly in line with each other forming the center of two sides of the square.

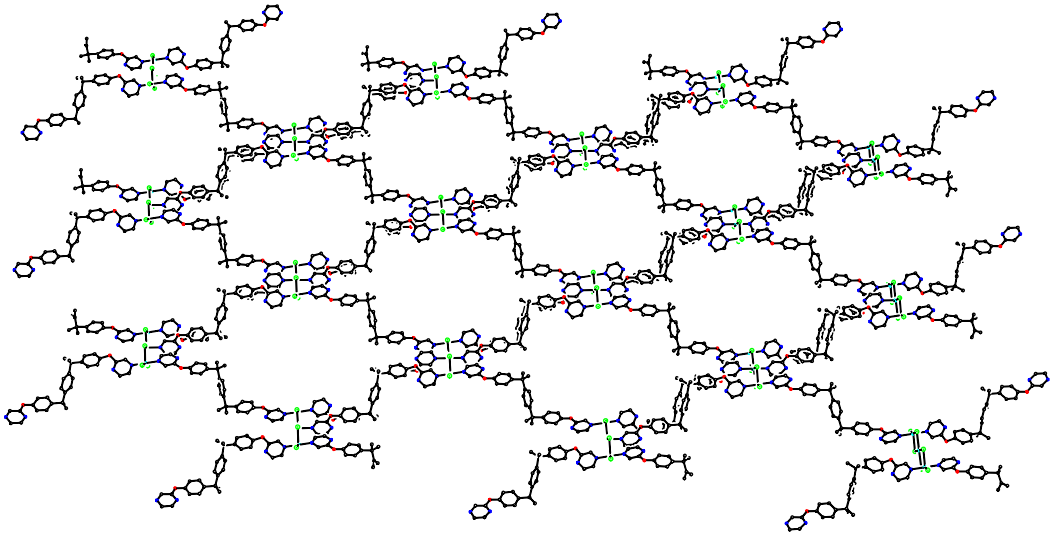


Figure 5.17 - *A section of the two-dimensional complex sheet of* ***5.16****, showing the connectivity and the cavities in the sheet.*

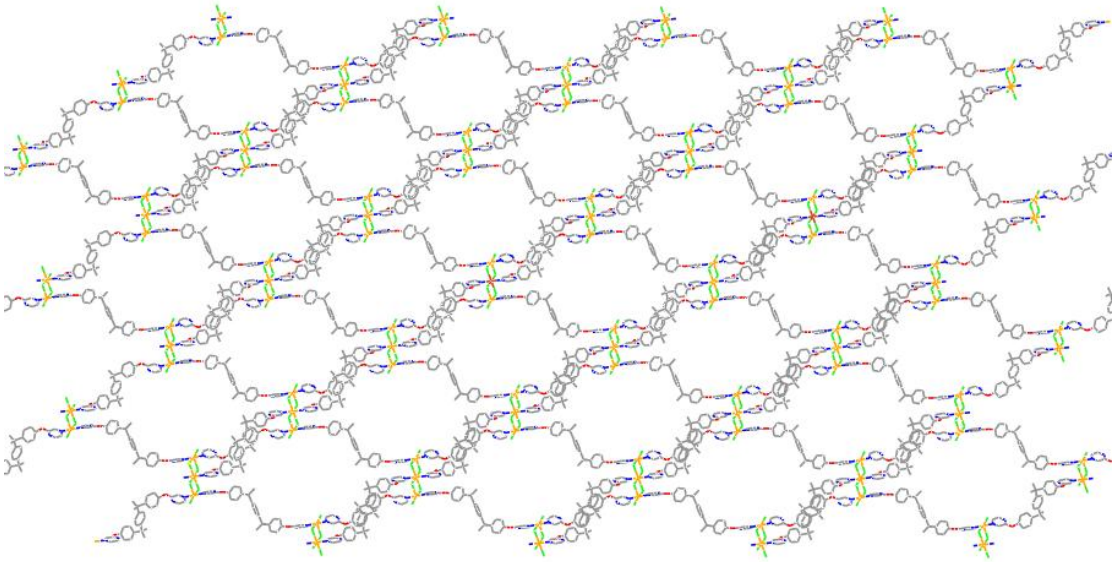


Figure 5.18 – *A larger section of the two-dimensional complex sheet of* ***5.16****.*

Other complexes with ligand ***5.11***

Complexation of ligand **5.11** with a variety of metal salts mainly gave precipitates that were unable to be recrystallised as they were insoluble in most common solvents. Consequently, only one complex crystallised and was able to be fully characterised by X-ray crystallography. A few of these precipitates were further analysed by elemental analysis and are discussed below.

A green crystalline precipitate was obtained from reaction of ligand **5.11** with $Cu(ClO_4)_2$ that analysed as a M_2L compound. Since the ligand can bind up to four metal atoms in total, but is more likely to coordinate to only two metal atoms through the least hindered nitrogen atoms, it is most likely to be a discrete complex. However, a polymeric structure is possible that is composed of M_2L units that are linked together by bridging perchlorates or solvent molecules.

The product of ligand **5.11** with $PdCl_2$ gives an immediate yellow precipitate that analyses as a ML compound. A orange precipitate formed immediately on combination of ligand **5.11** with $Pd(PhCN)_2Cl_2$ that analyses as a M_2L compound, which could be either a discrete complex or polymeric.

Complexes with ligands 5.12 and 5.13

Ligands **5.12** and **5.13** were reacted with a variety of different metal salts, viz $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $Pd(PhCN)_2Cl_2$, $ZnCl_2$ and $ZnBr_2$. Complexation of most of these metals with both ligands gave precipitates that were either insoluble or unable to be recrystallised. Consequently, no crystals suitable for X-ray crystallography were produced. Sometimes X-ray quality crystals were grown for either the ligand and/or the metal salt straight from the mixed solution. This was how the X-ray structure of the quinoline substituted ligand **5.12** was obtained from crystals that were grown from a mixed solution of the ligand with copper nitrate.

Reaction of ligand **5.12** with $PdCl_2$ and $Pd(PhCN)_2Cl_2$ gave yellow precipitates on slow evaporation that analysed with 1:1 metal to ligand stoichiometries.

The precipitate obtained from the reaction of ligand **5.12** with $CuCl_2$ analyses as a M_5L_2 compound. Since ligand **5.12** can only coordinate to a maximum of two metal atoms per ligand it is likely that the structure is discrete with a complicated copper chloride cluster made up of five metal atoms. Conversely the complex could be polymeric with ligand molecules bridged by copper chloride clusters. It must be noted that this type stoichiometry obtained is not necessarily representative of the whole sample.

Elemental analyses were carried out on the two palladium complexes made with ligand **5.13**. Ligand **5.13** was reacted with $PdCl_2$ producing a yellow precipitate that analysed as a ML_2 compound suggesting the formation of a discrete complex. Reaction of ligand **5.13** with $Pd(PhCN)_2Cl_2$ analysed as a M_2L compound suggesting the possible formation of a discrete complex or a palladium coordination polymer with Pd_2Cl_4 square motifs bridging together the ligands.

Reaction of ligand **5.13** with CuI revealed the formation of an intriguing ML_3 compound. Although a structure with this unusual ratio is possible, it is unlikely and therefore suggests that the sample taken may not be representative of the sample as a whole and suggests a mixture of products.

Despite numerous attempts no crystals of complexes were able to be obtained with the quinoline and quinoxaline substituted Bisphenol P ligands. The reasons as to why these

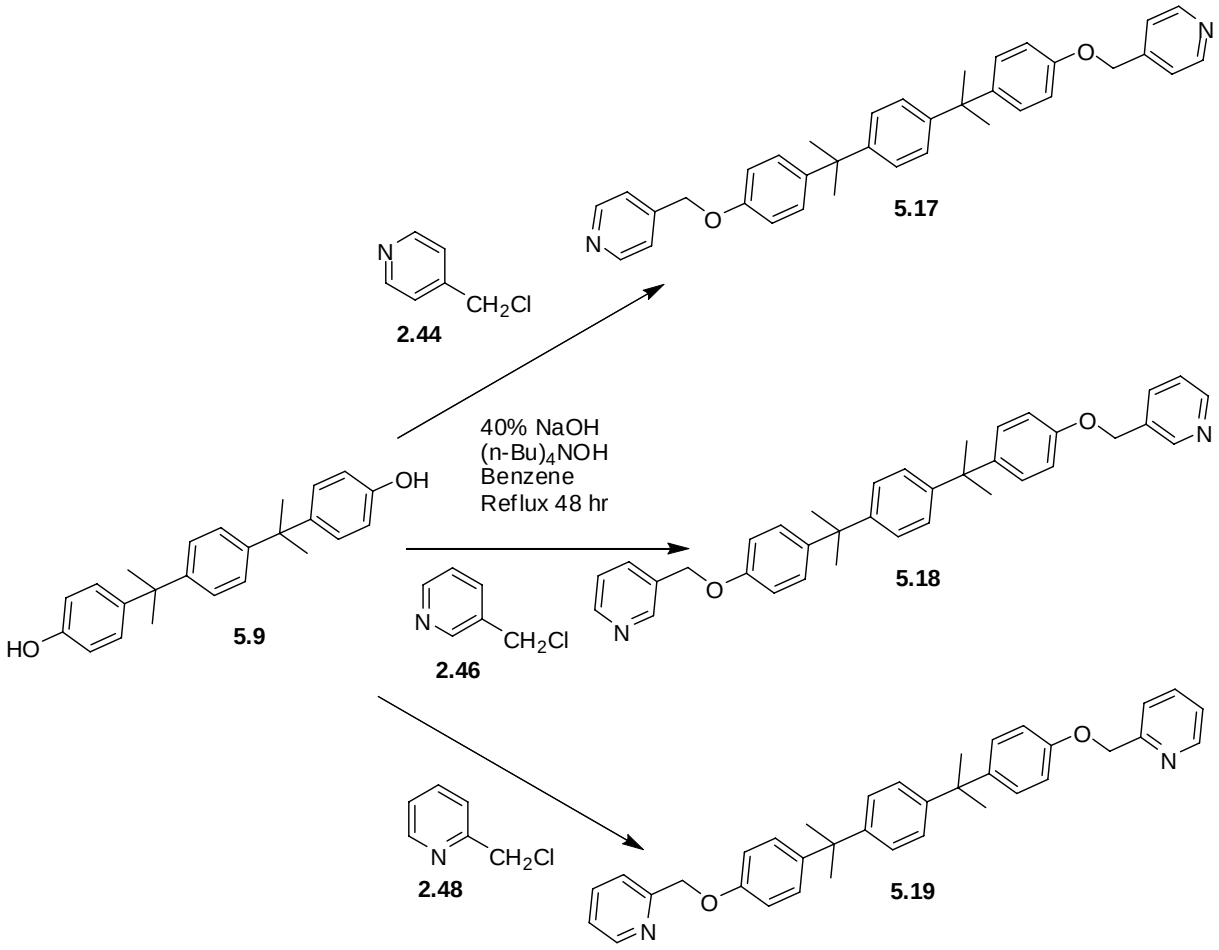
ligands with the larger heterocyclic ring systems did not crystallise as readily as the other Bisphenol P derived ligands are unknown. Perhaps the answer to this question lies in the chosen conformation of the ligands in the solid state. The conformation of the quinoline substituted ligand **5.12** had the nitrogen atoms pointing inwards towards the central phenylene spacer group, because the quinoline rings are perpendicular to the attached benzene rings. Consequently, in order for the nitrogen atoms to bind to metals the quinoline rings would have to twist around to be almost coplanar with the attached benzene rings. This more planar conformation would allow the coordination of metal atoms with less steric hindrance.

Synthesis of the Bisphenol P based -CH_2O- spaced ligands

To further analyse the use of Bisphenol P as a ligand core, three more ligands were synthesised from the Bisphenol P backbone with a spacer group containing two atoms, instead of just one. The two atom spacer group was composed of a methyleneoxy group that was positioned between the benzene ring and a 2-, 3- or 4-substituted pyridine ring of the ligand. It is anticipated that addition of a two atom spacer group to the Bisphenol P derived ligand may add more flexibility to the ligand allowing for the formation of more complex and interesting compounds, such as cages and helicates. Over the years, the Steel group has synthesised and explored many ligands with methyleneoxy spacer group extensions around many different aromatic cores with great success. Therefore it was logical to add a similar two atom spacer group to the Bipshenol P derived ligands that already contain a phenylene spacer group and explore these ligands as synthons in metallosupramolecular chemistry.

The three methyleneoxy spaced ligand synthesised from the Bipshenol P precursor are shown in Scheme 5.3. The ligands **5.17**, **5.18** and **5.19** were synthesised via a phase-transfer-catalysed (PTC) alkylation reaction in a method analogous to Hartshorn.[102, 172] The double alkylation of Bisphenol P with three isomeric chloromethylpyridines gave crude ligands **5.17**, **5.18** and **5.19** that were subsequently recrystallised from petroleum ether/ethyl acetate to give crystalline cream solids. Ligand **5.17** was isolated in a modest yield of 68%, whereas ligands **5.18** and **5.19** gave better yields of 82% and 80%, respectively.[113] Subsequently, all three ligands were fully characterised and crystals

suitable for X-ray crystallography were grown of all three methyleneoxy spaced ligands.



Scheme 5.3 – *Synthesis of new ligands **5.17**, **5.18** and **5.19** derived from the Bisphenol P core.*

Crystal structure of ligand 1,4-di(2-(4-(4-pyridylmethoxy)phenyl)prop-2-yl)benzene, 5.17

Crystals of ligand **5.17** suitable for X-ray crystallography were obtained by slow evaporation of the mother liquor from the recrystallisation. Ligand **5.17** crystallises in the triclinic space group P-1 with half a ligand molecule and half a water molecule in the asymmetric unit. The two halves of the ligand are related by a centre of inversion positioned at the centroid of the central phenyl ring. An X-ray crystal structure of the full ligand **5.17** is shown in figure 5.19 with the hydrogen atoms omitted for clarity. The doubly extended ligand **5.17** has a zig-zag shaped conformation in which each of the

aromatic groups is almost perpendicular to the adjacent one. The two benzene rings that flank the central benzene spacer ring lie perpendicular to it. The pyridine rings are also perpendicular to the closest benzene rings. The two nitrogen donor atoms are pointing outwards. The introduction of a phenylene spacer group and a two-atom spacer group extends the separation between terminal nitrogen donor atoms to 23.876Å. This is the largest distance between nitrogen donor atoms of all the Bisphenol P backboned ligands that have been crystallised so far.

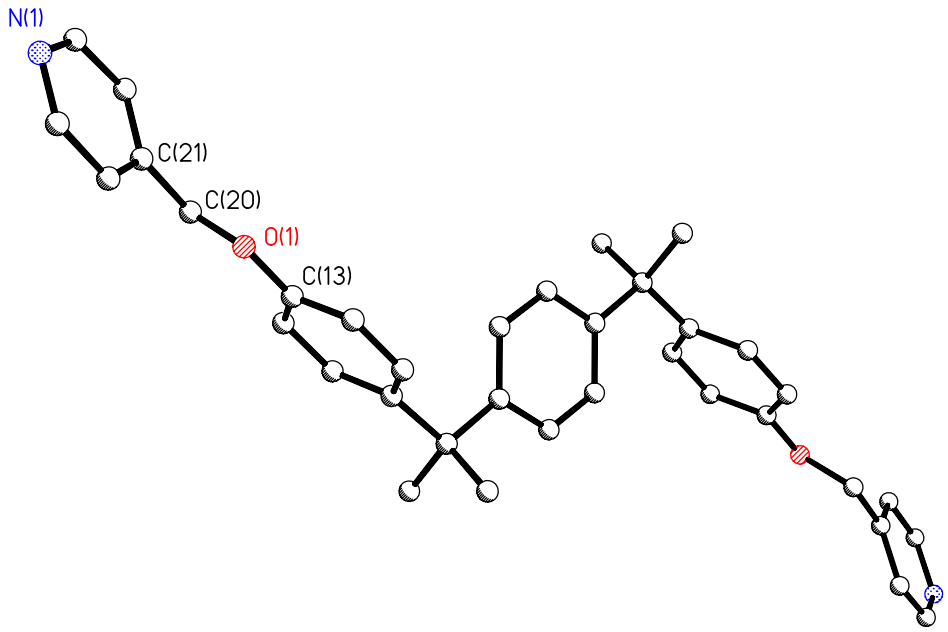


Figure 5.19 - *X-ray crystal structure of ligand* ***5.17****, with the hydrogens omitted for clarity. Selected bond lengths (Å) and angles (°): C13-O1 1.381(2), O1-C20 1.427(2), C20-C21 1.505(3), C13-O1-C20 117.1(2), O1-C20-C21 108.0(2).*

In the extended structure the water molecules hydrogen bond to the nitrogen atoms to form chains of ligands linked by water molecules. The ligand/water molecule chains adopt an interesting stepped staircase topology as illustrated in figure 5.20.

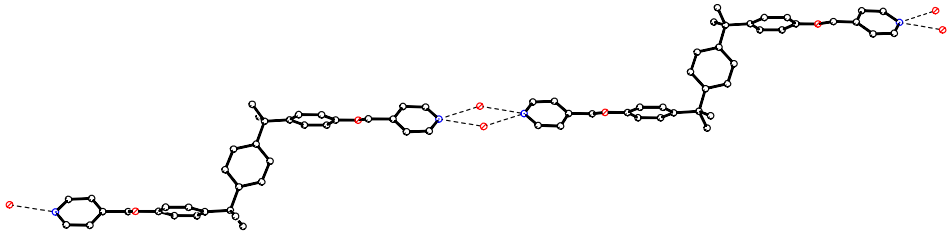


Figure 5.20 – *Illustration of the hydrogen bonded ligand/water molecule chains seen in ligand* ***5.17****, in which the hydrogen atoms have been removed for clarity.*

Crystal structure of ligand 1,4-di(2-(4-(3-pyridylmethoxy)phenyl)prop-2-yl)benzene, 5.18

Colourless crystals of ligand **5.18** suitable for X-ray crystallography were formed from a solution containing the mother liquor on slow evaporation. It crystallises in the monoclinic space group $P2_1/n$ with half a molecule in the asymmetric unit, with a crystallographically imposed centre of inversion positioned at the centroid of the central phenyl ring. The crystal structure of the full doubly extended ligand **5.18** is shown in figure 5.21, with the hydrogens omitted for clarity. The ligand adopts an 'S'-shaped conformation as a consequence of the phenylene spacer unit with each of the aromatic rings almost perpendicular to one another. The two benzene rings that flank the central phenylene spacer ring are perpendicular to the spacer unit. The pyridine rings are also perpendicular to the closest benzene rings. The nitrogen atoms on the pyridine rings are facing in opposite directions outwards from one another. The two-atom methyleneoxy spacer group adopts a trans-periplanar arrangement, which is reflected in the C-C-O-C torsional angle of 178.3°. The addition of a phenylene spacer group as well as a two-atom spacer group extends the distance between nitrogen donor atoms to 23.132Å.

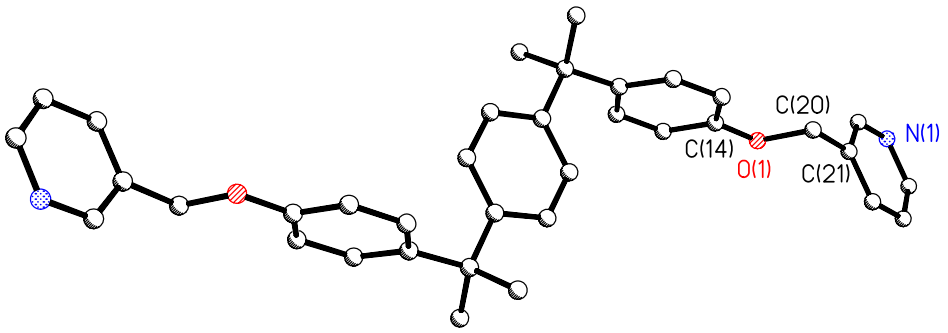


Figure 5.21 – *X-ray crystal structure of ligand* ***5.18****, with the hydrogens omitted for clarity. Selected bond lengths (Å) and angles (°): C14-O1 1.374(2), O1-C20 1.434(2), C20-C21 1.498(3), C14-O1-C20 117.0(1), O1-C20-C21 106.7(2).*

In the crystal packing there are sheets of ligands that interact though numerous hydrogen bonding interactions. Edge-to-face interactions are observed between the benzene rings and the pyridine rings of adjacent ligands within a sheet (2.644Å) and various other hydrogen bonding interactions such as C-H···π bonding interactions occur between other sheets of ligands.

Crystal structure of ligand 1,4-di(2-(4-(2-pyridylmethoxy)phenyl)prop-2-yl)benzene, 5.19

Pale yellow crystals of ligand **5.19** were grown from a solution of the ligand and copper nitrate in a methanol/dichloromethane solution. The doubly extended 2-substituted pyridine ligand **5.19** crystallises in the monoclinic space group $P2_1/c$, with a crystallographically imposed centre of inversion positioned at the centroid of the central phenyl ring. The X-ray crystal structure of ligand **5.19** is shown in figure 5.22 with the hydrogens removed for clarity. The conformation of ligand **5.19** is very similar to that of the 3-substituted isomer **5.18** described above. Ligand **5.19** has the same overall conformation with each of the aromatic arene groups almost perpendicular to each other. Once again the benzene rings that flank the central phenylene ring are perpendicular to the spacer unit and the pyridine rings are also almost perpendicular to the attached benzene rings. The nitrogen atoms are twisted to point outwards in opposite directions directly away from one another, similar to that seen in ligand **5.18**.

As a consequence of these similarities between the structures, the two-atom methyleneoxy spacer group also has the same trans-periplanar arrangement with an almost identical torsional angle of 178.4°. As expected the nitrogen donor atoms are now separated by a shorter distance of 19.690Å, as a consequence of the substitution in the 2-positions of the pyridine rings.

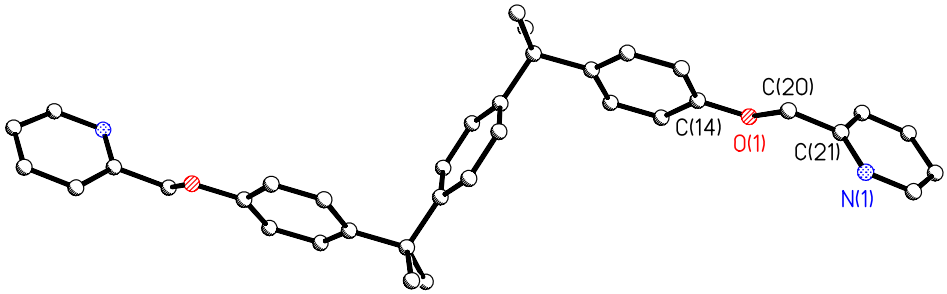


Figure 5.22 - *X-ray crystal structure of ligand* ***5.19****, with the hydrogens omitted for clarity. Selected bond lengths (Å) and angles (°): C14-O1 1.381(1), O1-C20 1.425(1), C20-C21 1.503(2), C21-N1 1.338(2), C14-O1-C20 117.11(9), O1-C20-C21 107.6(1), N1-C21-C20 116.1(1).*

In the extended structure there are various hydrogen bonding interactions between ligand molecules. Weak edge-to-face interactions are observed between benzene rings and pyridine rings (2.689Å). There are no observed π-π interactions.

Complexes with ligand 5.17

Complexation of ligand **5.17** was attempted with many different cobalt, copper, silver, palladium and zinc salts. Unfortunately, reaction of ligand **5.17** with metal salts only gave precipitates or crystalline solids that, despite several attempts, were unable to be recrystallised from most common solvents, including DMSO and were therefore analysed no further. Blue plate-like crystals were generated from the reaction of $Cu(NO_3)_2$ with ligand **5.17** that were put up for X-ray crystallography. However the thin plate-like crystals were stacked on top of each other and highly twinned and therefore the structure was unable to be solved.

Elemental analyses were carried out on a couple of the copper complexes made with ligand **5.17**. Ligand **5.17** was reacted with $Cu(NO_3)_2$ and $Cu(ClO_4)_2$ to give blue crystals and a blue solid, respectively. Both these complexes analysed as a ML_2 compound. This ratio of components suggests the formation of a discrete complex composed of two ligands around a metal centre or more probably a polymeric complex.

Elemental analyses were also carried out on the complexes formed with the palladium metal salts. Ligand **5.17** was reacted with $PdCl_2$ and $Pd(PhCN)_2Cl_2$ producing a peach precipitate and a yellow crystalline solid, respectively. Both these complexes analysed with a 1:1 ratio.

Reaction of ligand **5.17** with $CoBr_2$ produced a blue precipitate on slow evaporation that analysed as a M_3L_3 compound. Since each ligand can only bind two metal atoms this ratio suggests the possible formation of a discrete structure. Such discrete M_3L_3 structures are not uncommon. In fact during her PhD, Jennifer Zampese made a M_3L_3 macrocycle with a two armed bridging ligand that had a truncated triangular shape and encapsulates a solvent molecule.[109] A blue precipitate formed on reaction of $CoCl_2$ with ligand **5.17** analysed as a M_2L compound.

Complexes with ligand 5.18

*Crystal structure of the complex with $AgPF_6$ (**5.20**)*

Ligand **5.18** was dissolved in chloroform and layered upon a solution of silver hexafluorophosphate dissolved in acetone. Ethyl acetate was slowly diffused into the reaction mixture and slow evaporation over time afforded perfect block-like crystals on the sides of the vial that were suitable for X-ray crystallography. X-ray analysis revealed a one-dimensional polymer that crystallises in the triclinic space group P-1. The asymmetric unit contains two independent half-ligands, one silver atom, one hexafluorophosphate anion, one acetone solvent molecule and two ethanol solvent molecules. One of the ethanol molecules is coordinated to the silver atom through the oxygen atom, while the other ethanol molecule and acetone molecule remain non-coordinated. A section of the one-dimensional polymer is shown in figure 5.23, which is grown to show the connectivity around the silver atom and its coordination to an

ethanol molecule. The hydrogens and other solvent molecules have been omitted for clarity in figure 5.23.

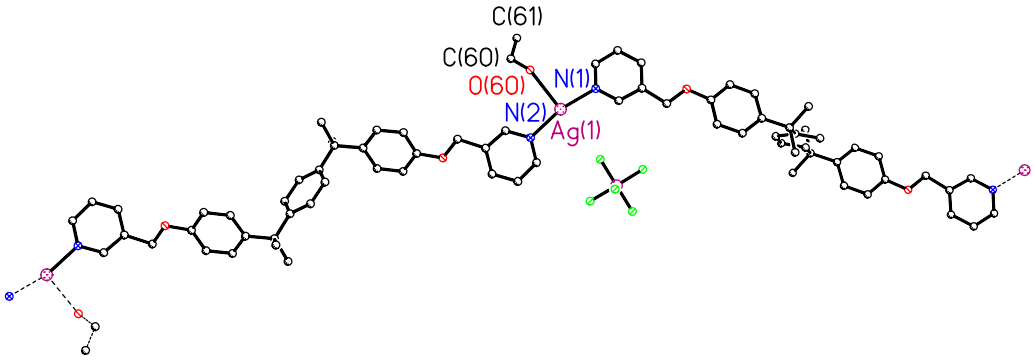


Figure 5.23 – *A section of the silver one-dimensional polymer* ***5.20****. Selected bond lengths (Å) and angles (°): Ag1-N1 2.145(3), Ag1-N2 2.151(4), Ag1-O60 2.563(6), O60-C60 1.308(9), C61-C60 1.456(10), N1-Ag1-N2 167.0(2), N1-Ag1-O60 97.9(2), N2-Ag1-O60 95.1(2), C60-O60-Ag1 142.9(7), O60-C60-C61 118.4(8).*

The conformation of the ligand in complex **5.20** is similar to that of free ligand **5.18** in the solid state, adopting a similar zig-zag topology. The two benzene rings that flank each side of the central phenylene of the ligand are almost perpendicular to the central phenylene ring and the two-atom spacer group also has the same trans-periplanar arrangement. There is a slight disorder in the positioning of the silver atom, which is located 92% of the time in one position and 8% of the time in another. The non-coordinated ethanol molecule has only 50% occupancy.

The silver atom coordinates to two separate ligands with a bent geometry of 167.0°, which is not uncommon in such silver complexes. Subsequently, each ligand bridges together two metal atoms. The hexafluorophosphate anion is not coordinated to the main chain. The Ag-N bond lengths are 2.145Å and 2.151Å, which are within the range of other silver(I) complexes. The coordination geometry of the silver atom, which is also coordinated to an ethanol molecule through the oxygen atom, is best described as a 'T-shaped' geometry. The small deviation from linearity between the two nitrogen atoms and the silver atom is due to the presence of the coordinated ethanol. The bond distance between the silver atom and the coordinated oxygen atom from the ethanol solvent molecule is 2.563Å.

Complex **5.20** propagates in an undulating wave-like fashion in one-dimension through centres of inversion within the ligands. This is clearly illustrated in a larger section of the polymer in figure 5.24, with the hydrogens and non-coordinated solvent molecules omitted for clarity. The resulting coordination polymer **5.20** is composed of ligands that bridge silver atoms with an alternating arrangement of hexafluorophosphate anions and ethanol groups along the polymer chain. The hexafluorophosphate anion only interacts weakly with the nearby silver atom.

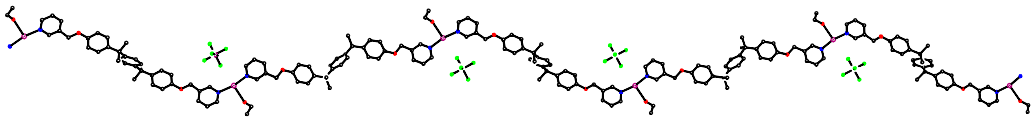


Figure 5.24 – *A larger section of polymer **5.20** illustrating the undulating wave-like topology.*

The silver chains pack closely in the crystal lattice with the acetone molecules and the non-coordinated ethanol molecules interacting extensively through various short contacts to fill voids in the crystal lattice. The coordinated ethanol molecule further interacts through hydrogen bonding with the non-coordinated ethanol molecule. There are only a few hydrogen bonding interactions between silver chains in the extended structure. No π-π stacking interactions were observed.

*Other complexes with ligand **5.18***

Ligand **5.18** was reacted with a variety of metals salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $Pd(PhCN)_2Cl_2$, $ZnCl_2$ and $ZnBr_2$. under various conditions. One silver complex was obtained and analysed by X-ray crystallography as detailed above. Unfortunately, no other complexes were able to be crystallised for full structure determination by X-ray analysis.

Elemental analysis revealed probable 1:1 ratios with $CoBr_2$, $Cu(ClO_4)_2$ and $Pd(PhCN)_2Cl_2$ metal salts and ligand **5.18**. This ratio is plausible and could indicate either a discrete structure or one-dimensional polymer. A polymeric structure is most likely, due to the desired conformation of the ligand in the solid state and this is also the structure that formed with $AgPF_6$.

Reaction of ligand **5.18** with $CoCl_2$ gave a blue crystalline solid that analysed as a M_2L compound. Since ligand **5.18** can bind up to a maximum of two metal atoms this stoichiometry is possible for the formation of a discrete complex composed of a ligand coordinated to two cobalt atoms or perhaps some kind of polymer complex. A $Cu(NO_3)_2$ complex also analysed as a M_2L compound.

Reaction of ligand **5.18** with $Cu(ClO_4)_2$ produced a blue solid that analysed as a ML_2 compound.

Complexes with ligand 5.19

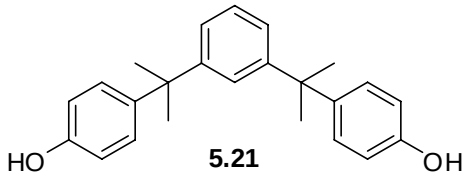
Complexation of ligand **5.19** was attempted with many different metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $Pd(PhCN)_2Cl_2$, $ZnCl_2$ and $ZnBr_2$. Regrettably crystals suitable for X-ray analysis were unable to be grown with any of these metal salts. Precipitates formed almost immediately or not long after mixing of the solutions, which were insoluble. Sometimes instead of complexation, crystals were grown of either the ligand and or metal salt straight from the mixed solution. This was how the ligand **5.19** was able to be fully characterised.

A fine blue/green precipitate was produced on reaction of ligand **5.19** with $CuCl_2$. The compound analyses with a 1:1 ratio suggesting a discrete or polymeric structure. There is no presence of any solvent molecules in the elemental analysis.

Reaction of ligand **5.19** with $Cu(ClO_4)_2$ gave a crystalline solid that analysed as a M_2L compound with one acetone solvent molecule.

Synthesis of the Bisphenol M based -O- spaced ligands

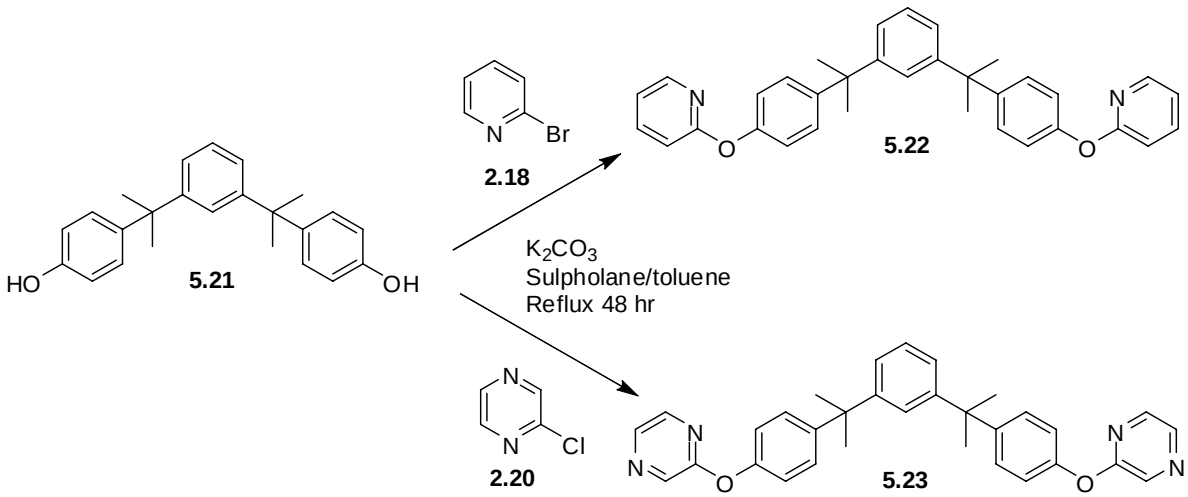
Another set of two-armed bridging ligands based around a Bisphenol M backbone was designed and synthesised as synthons for metallosupramolecular chemistry. The new Bisphenol M ligand precursor was reacted with the same haloazines and chloromethylpyridines as the Bisphenol P based ligands to generate new symmetrical bridging ligands. The ligand precursor 4,4'-(1,3-phenylenediisopropylidene)bisphenol, commercially known as Bisphenol M, is almost identical to Bisphenol P. Both ligand precursors have a central phenylene spacer group that is inserted between the two aromatic benzene rings and two propane groups of the ligand. The only difference between the two precursors is the substitution positions of the ligand arms around the central spacer unit. The Bisphenol P derived ligands have a 1,4-substitution pattern around the central phenylene ring, whereas the Bisphenol M derived ligands have a 1,3-substitution pattern around the central phenylene ring, as illustrated in the structure of Bisphenol M in figure 5.25.



5.21

Figure 5.25 – *Structure of Bisphenol M.*

Once again all the one-atom oxygen spaced ligands with the Bisphenol M backbone were synthesised via the same nucleophilic substitution reactions employed throughout this thesis by refluxing in a sulpholane/toluene solvent mixture.[112] The synthesis of the first two ligands derived from the Bisphenol M precursor is outlined in Scheme 5.4. The two haloazines 2-bromopyridine (**2.18**) and 2-chloropyrazine (**2.20**) were substituted onto the Bisphenol M precursor to generate new ligands **5.22** and **5.23**, respectively. The crude ligands were recrystallised from an acetone/water mixture to produce pure white solids in 23% and 94% yields, respectively.[113] Both of the ligands were fully characterised and crystals of the pyrazine substituted ligand **5.23** were analysed by X-ray crystallography.



Scheme 5.4 – *Synthesis of ligands **5.22** and **5.23** from Bisphenol M.*

Crystal structure of ligand 1,3-di(2-(4-(2-pyrazinyloxy)phenyl)prop-2-yl)benzene, 5.23

Thin colourless plates of ligand **5.23** were grown from a solution of ligand **5.23** and zinc bromide. This compound crystallises in the monoclinic space group $P2_1/c$ with a whole molecule in the asymmetric unit. The X-ray crystal structure of ligand **5.23** is shown in figure 5.26, where the hydrogens are omitted for clarity. Ligand **5.23** has more of an extended shape, in comparison to the zig-zag conformations of the Bisphenol P backboned bridging ligands. The arms of ligand **5.23** stretch further outwards thereby eliminating any apparent internal zig-zag conformation in the ligand itself. In this compound the pyrazine rings lie almost perpendicular to the attached benzene rings, with the internal nitrogen atoms pointing inwards towards the centre of the attached benzene ring. Both of the internal nitrogen atoms on the pyrazine substituted ligand are pointing in the same direction inwards, whereas the less hindered distal nitrogen atoms are pointing outwards. The orientation of the pyrazine rings is reflected in the low N-C-O-C torsional angles of 16.2° and 17.1°. Once again the introduction of the phenylene spacer group increases the separation between nitrogen atoms in ligand **5.23**. The distance between the two internal nitrogens is 16.257Å, while the distal nitrogens have a much longer separation of 21.373Å. It is anticipated that the less hindered distal nitrogen donor atoms will more easily coordinate to metal atoms.

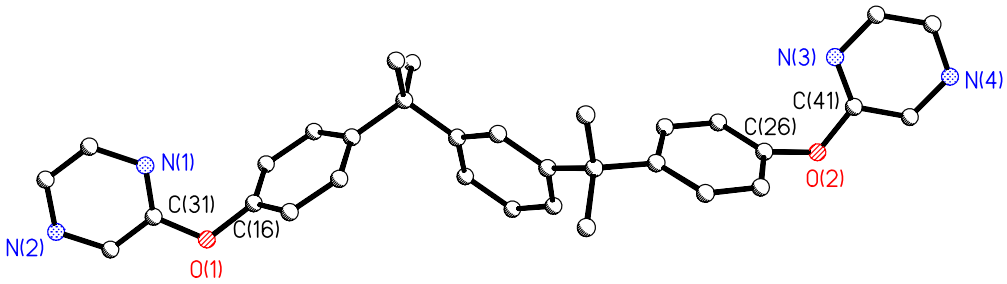
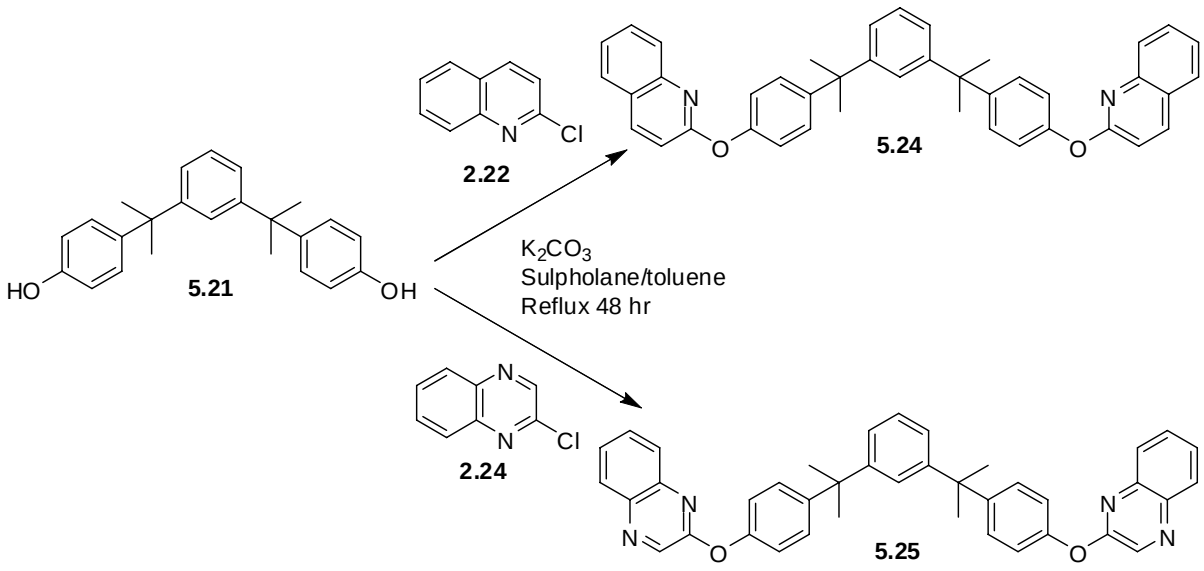


Figure 5.26 – *X-ray crystal structure of ligand* ***5.23****. Selected bond lengths (Å) and angles (°): C16-O1 1.403(4), O1-C31 1.354(4), C31-N1 1.313(4), C26-O2 1.420(4), O2-C41 1.364(4), C41-N3 1.305(4), C31-O1-C16 118.0(3), N1-C31-O1 120.0(3), C41-O2-C26 120.0(3), N3-C41-O2 119.9(3).*

In the crystal packing there are sheets of ligands that pack together with various hydrogen bonding interactions within a sheet and between adjacent layers of sheets. Within a sheet there are π-π stacking interactions between pyrazine rings, as well as C-H···π bonding between a methylene hydrogen atom and the plane of the adjacent benzene ring (2.833Å). Furthermore the sheets of ligands stack together by numerous hydrogen bonding interactions, π-π stacking interactions and edge-to-face interactions.

The next two ligands synthesised from the Bisphenol M are outlined in Scheme 5.5. The synthesis is the same as that shown in the previous Scheme 5.4. The diaryl ether linkages on ligands **5.24** and **5.25** were synthesised via double nucleophilic aromatic substitution of precursor **5.21** with 2-chloroquinoline (**2.22**) and 2-chloroquinoxaline (**2.24**).[112] Recrystallisation of the crude ligands from an acetone/water mixture produced a yellow crystalline solid and an orange solid in reasonable yields of 80% and 78%, respectively.[113] Subsequently, both of the ligands were fully characterised. Crystals of both ligands were grown and the X-ray structures were determined to investigate their conformations in the solid state.



Scheme 5.5 – *Synthesis of ligands **5.24** and **5.25** via double nucleophilic aromatic substitution.*

Crystal structure of ligand 1,3-di(2-(4-(2-quinolyloxy)phenyl)prop-2-yl)benzene, 5.24

Slow evaporation of the mother liquor produced perfect block-like crystals of **5.24**. The X-ray crystal structure of ligand **5.24** is depicted in figure 5.27 with the hydrogens removed for clarity. Ligand **5.24** crystallises in the triclinic space group P-1 with the whole ligand in the asymmetric unit. There is no observed symmetry in ligand **5.24** as a consequence of the conformation of the ligand. In addition, the conformation of the quinoline substituted ligand in the solid state is quite different to that of any other larger ligands described in this thesis. Ligand **5.24** seems to twist around on itself to give a relatively compact structure as opposed to having the extended shape adopted by many of the other ligands. Each of the aromatic rings adopts a perpendicular orientation to adjoining aromatic rings to generate a hook-shaped conformation in the solid state. A space-filling diagram of the ligand more clearly illustrates the hook-like conformation of ligand **5.24**. The two quinoline rings are positioned perpendicular to the attached benzene rings with the nitrogen donor atoms oriented to point inwards towards the internal cavity. As a consequence the separation between nitrogen donor atoms is a mere 10.473Å. This small distance between nitrogen atoms is short in comparison to all the other phenylene extended ligands in this chapter. Furthermore, as a consequence of the twisting of ligand **5.24**, one of the nitrogen atoms is nestled inside a cavity of its

own, which is more clearly seen in the space-filling diagram in figure 5.28. Due to the size of the cavity this nitrogen atom is unlikely to coordinate to any metals in this adopted conformation.

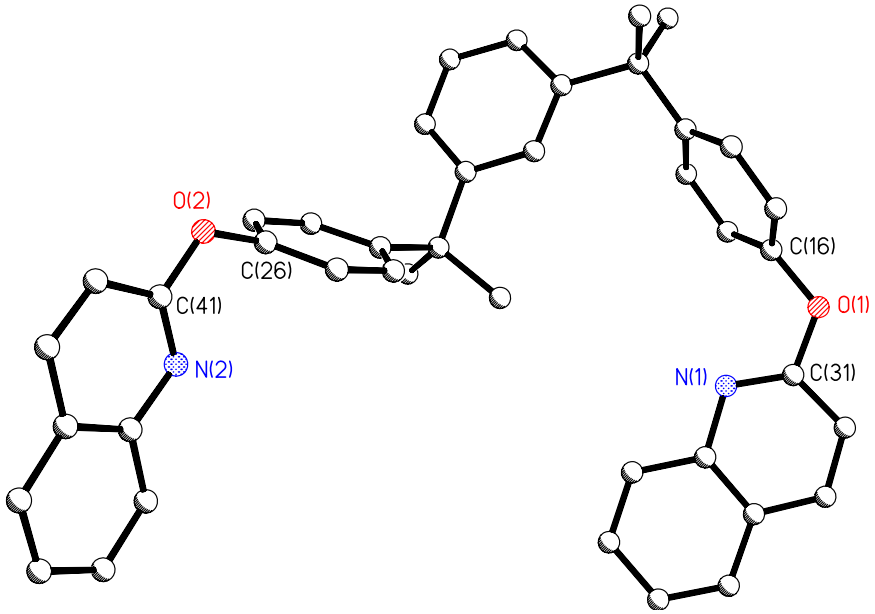


Figure 5.27 - *X-ray crystal structure of ligand* ***5.24****. Selected bond lengths (Å) and angles (°): C16-O1 1.406(2), O1-C31 1.368(2), C31-N1 1.302(2), C26-O2 1.413(2), O2-C41 1.368(2), C41-N2 1.298(2), C31-O1-C16 119.0(1), N1-C31-O1 119.9(2), C41-O2-C26 118.7(1), N2-C41-O2 120.0(2).*

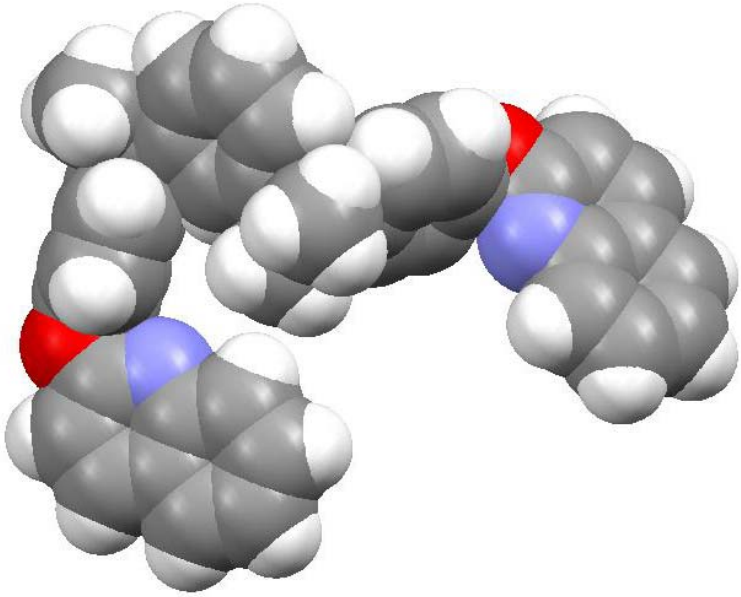


Figure 5.28 – *A space-filling diagram of ligand* ***5.24*** *that clearly accentuates the unusual hook conformation of the ligand in the solid state.*

In the extended structure the ligand molecules stack together via numerous hydrogen bonding interactions. There are many edge-to-face interactions between quinoxaline rings and benzene rings that range between 2.661Å-2.805Å.

Crystal structure of ligand 1,3-di(2-(4-(2-quinoxalinyloxy)phenyl)prop-2-yl)benzene, 5.25

Colourless crystals of ligand **5.25** were grown from a solution of ligand **5.25** and cobalt chloride in acetone. The compound crystallises in the triclinic space group P-1 with half a ligand molecule in the asymmetric unit. The central phenylene ring/spacer group lies on a crystallographic centre of inversion that generates the full ligand, as shown in figure 5.29. There is some disorder in the central benzene ring around the inversion centre, which is not shown in figure 5.29. The disorder is seen in the meta-substitution of the benzene spacer group. This type of meta disorder in a phenyl ring is not unheard of and has recently been seen and described by Tian et al. in a zinc complex with the meta-substituted ligand 1,3-bis(imidazol-1-ylmethyl)benzene.[287] Tian et al. were synthesising MOFs (metal organic frameworks) using the meta-substituted ligand and found the same disorder in the central benzene ring of the ligand in the zinc complex as seen in ligand **5.25**.

Ligand **5.25** adopts a zig-zag shaped conformation as a consequence of the phenylene spacer unit with each of the aromatic rings almost perpendicular to one another. This zig-zag shape of the ligand itself has been seen a few times in the phenylene extended ligands described in this chapter. In ligand **5.25** the quinoxaline heterocyclic groups are almost perpendicular to the attached benzene ring with the two internal nitrogen atoms pointing inwards towards the centre of the benzene rings and the central spacer benzene group with a separation of 14.949Å. The less hindered distal nitrogen atoms are oriented to point outwards to give a much larger separation of 20.347Å. Consequently the less hindered nitrogen atoms are more likely to coordinate to metal atoms.

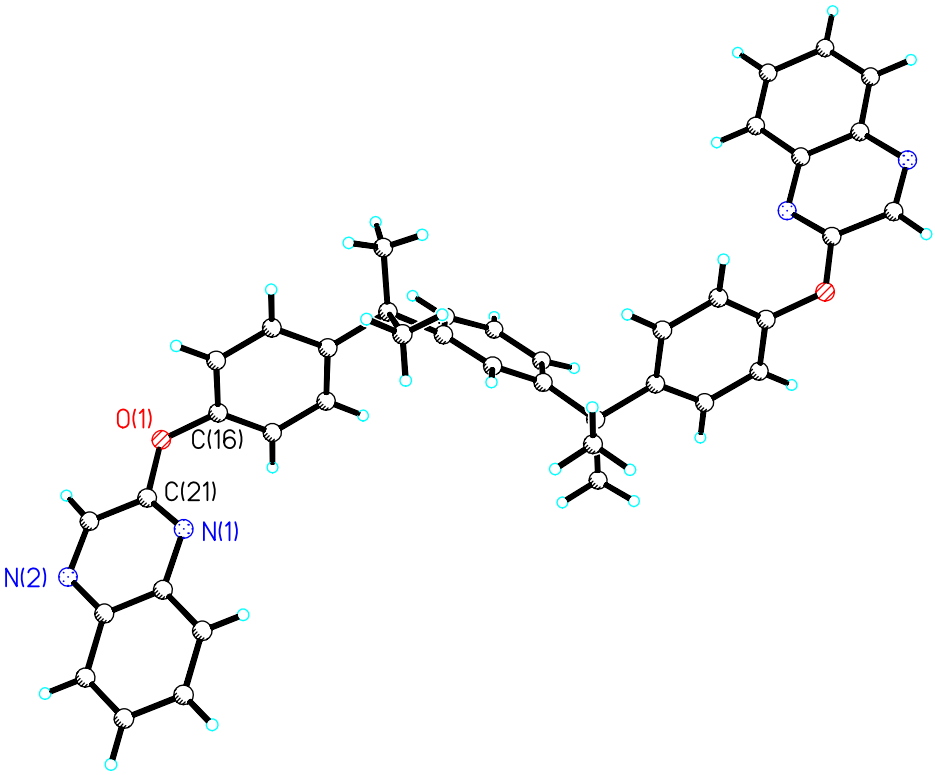


Figure 5.29 – *X-ray crystal structure of ligand* ***5.25****. The disorder associated with the meta-substitution of the central benzene ring is not shown. Selected bond lengths (Å) and angles (°): C16-O1 1.402(3), O1-C21 1.351(3), N1-C21 1.287(3), C21-O1-C16 119.1(2), N1-C21-O1 121.8(2).*

A literature search revealed only one set of compounds that incorporate the Bisphenol M binding domain in its core structure. These compounds were synthesised by the same group that also constructed the isomeric phosphite caged cryptand molecules with Bisphenol P and PCl_3 discussed earlier. Bauer et al. obtained X-ray structures of two of the cage-like macrobicyclic isomers similar to that generated with Bisphenol P, but with Bisphenol M.[288] Interestingly one other discrete product was also generated from the reaction of Bisphenol M and PCl_3 that had quite a different structure. Subsequently, X-ray analysis revealed a Bisphenol M unit that is capped at each end by a small macrocyclic Bisphenol M unit through the phosphite atom.

There were no other closely related ligands in the literature to the Bisphenol M backboned ligands **5.22**, **5.23**, **5.24** and **5.25**. However there are some ligands that display structural similarities to the Bisphenol M based ligands by containing a 1,3-substitution pattern around a benzene ring somewhere in the ligand structure. Shown in figure 5.30 are some examples of such ligands that contain the Bisphenol M binding domain in its core structure. Ligands **5.26**-**5.28** are three such ligands that display a 1,3-substitution pattern around a benzene ring somewhere in the ligand structure, although without the alcohol group substitution. Ligand **5.26** is a ligand that contains two meta-substitutions around a benzene ring that flank each side of a dithiabutanediyl (SCH_2CH_2S) bridge. Capacchione et al. generated a titanium complex from titanium tetrachloride and ligand **5.26** that displayed an octahedral geometry around the titanium metal atom, with the oxygen atoms *trans* to each other and the two sulfur atoms and two chlorine atoms *cis* with respect to each other.[289] This titanium complex was initially made in order to investigate its ability to polymerize styrene upon activation with MAO, which it did effectively to give isotactic styrene. In 2003 Schmitt et al. designed and synthesised the iminodiacetic acid ligand **5.27** and reacted it with $FeCl_3$ in the presence of $KHCO_3$.[290] The resulting complex displayed an unusual cation-π interaction between the α,α-dimethylbenzyl groups and the potassium ions. More recently, Axenov et al. made a hafnium dibenzyl complex with ligand **5.28**.[291] Once again this ligand contains the 1,3-substitution around a benzene ring within the ligand core structure. Axenov et al. synthesised the hafnium dibenzyl complex with ligand **5.28** as well as others in order to investigate their ability as catalysts for the polymerizations of ethylene and propylene.

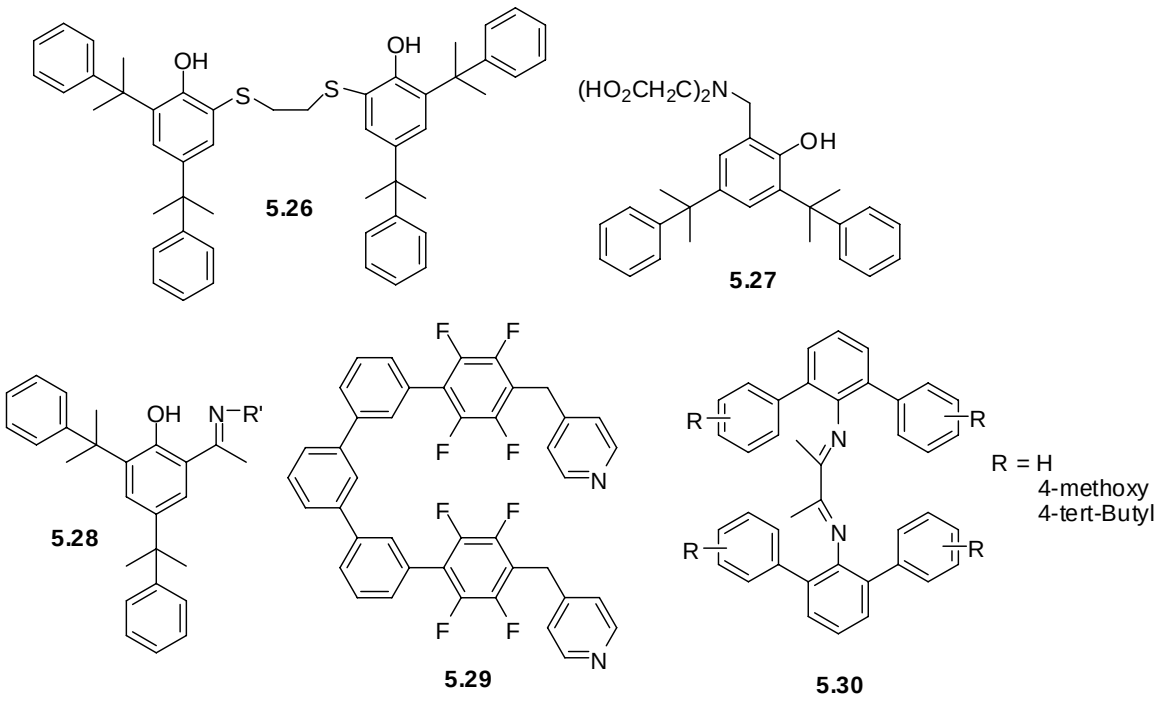


Figure 5.30 – *Examples of structurally related ligands to the Bisphenol M substituted ligands.*

If one removed the two propane groups that flank the central benzene ring of Bisphenol M, one would have a single bond between the 1,3-substitution of the flanking benzene rings. Ligands **5.29** and **5.30** are two examples of ligands designed around such a ligand core with nitrogen binding domains. Ligand **5.29** is an example of a ligand with quite a different structural core containing 4-pyridine units attached to a pentakis(m-phenylene) core. Fujita and co-workers reported the self-assembly of this ligand with $Pd(NO_3)_2$ into an achiral palladium macrocycle.[292] This macrocycle was found to undergo spontaneous catenation into a catenated complex when the concentration of D_2O in the solvent mixture is increased. Furthermore, in the catenated complex the two aromatic ligand strands are double-helicated to one another, which was seen in the X-ray structure. In 2001, Schmid et al. designed and synthesised a series of diimine ligands with ligand **5.30** that were reacted with $Pd(PhCN)_2Cl_2$.[293] The resulting palladium dichloro complexes were crystallised and analysed by X-ray crystallography. As expected the palladium(II) metal atoms coordinated to the bidentate diimine nitrogen atoms to form a series of discrete palladium complexes.

Complexes with ligand 5.22

The pyridine-substituted ligand **5.22** was reacted with only a small selection of metal salts due to the minimal amount of ligand isolated. Unfortunately, no crystals of complexes were able to be grown for X-ray crystallography. Mainly precipitates formed immediately upon complexation, due to the insolubility of the ligand in most solvents, which were found to often be just the ligand crashing out of solution. Furthermore, the few complexes isolated were insoluble in any solvents.

A yellow precipitate formed immediately on reaction of ligand **5.22** with $PdCl_2$. This precipitate was eventually filtered off after numerous attempts at recrystallisation with a variety of solvents with no success. The precipitate analysed as a ML_2 compound.

Slow evaporation of a solution containing ligand **5.22** and $CuCl_2$ produced a green solid. Unfortunately, the sample sent off for elemental analysis was found to be inconsistent with any reasonable structure, suggesting a mixture of products in the sample.

Complexes with ligand 5.23

*Crystal structure of the complex with $Cu(ClO_4)_2$ (**5.31**)*

Ligand **5.23** and copper perchlorate were dissolved in a solution of hot acetone and then allowed to cool down slowly. Slow evaporation over a few days of the blue solution gave clusters of blue crystalline material on the bottom of the vial. It was hard to extract a single crystal, because all the crystals were clustered into star-like arrangements on top of one another. Eventually a small thin blue crystal was found that was suitable for X-ray crystallography. Unfortunately, the thin crystals diffracted poorly and the structure obtained showed some disorder, giving a final R_1 value of 9.89%. However, despite this the X-ray crystal structure of complex **5.31** was still obtained and is described.

The X-ray crystal structure of **5.31** solved in the triclinic space group P-1. The asymmetric unit contains one ligand molecule, half a copper atom, a disordered perchlorate anion, two acetone molecules, one of which has half occupancy and possibly a water molecule. A view of the asymmetric unit showing the extended

connectivity of complex **5.26** is shown in figure 5.31, which also illustrates the disorder of the perchlorate anion. Excluded are the solvent molecules and hydrogen atoms.

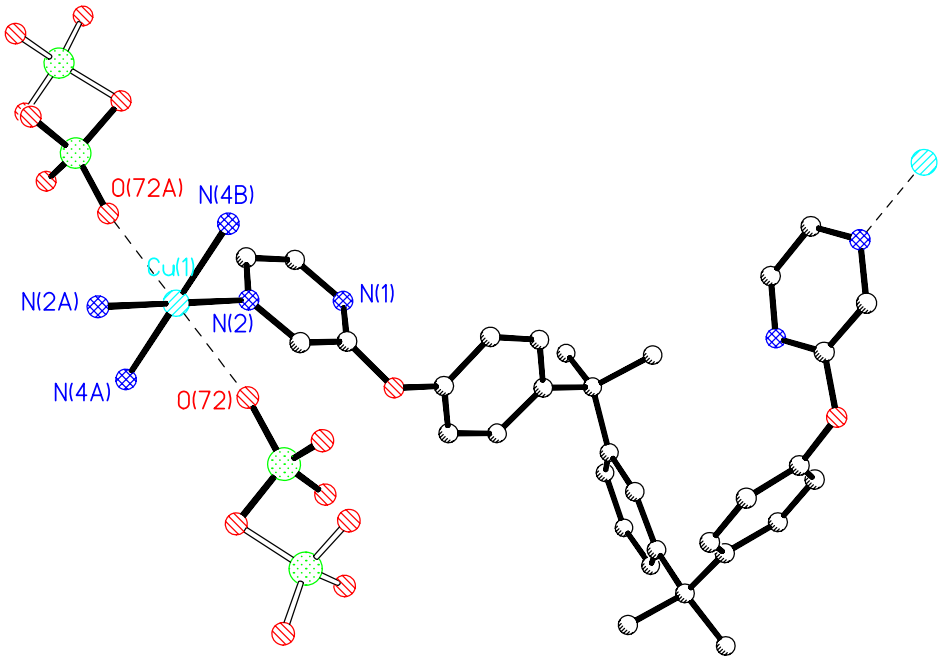


Figure 5.31 – *Contents of the asymmetric unit of complex* ***5.31****. Selected bond lengths (Å) and angles (°): Cu1-N2 2.025(5), Cu1-N4B 2.042(6), N2-Cu1-N2A 180.0(3), N2-Cu1-N4B 90.0(2), N4B-Cu1-N4A 180.0(1).*

The conformation of the pyrazine substituted ligand in complex **5.31** is somewhat different to the conformation of ligand **5.23** itself in the solid state. Surprisingly, the ligand adopts a similar hook-like conformation to the quinoline-substituted ligand **5.24** in the solid state. Each of the aromatic rings is almost orthogonal to the adjacent aromatic rings of the ligand. The two pyrazine rings lie perpendicular to the planes of the attached benzene rings with the two internal nitrogen atoms facing inwards towards the centers of the attached benzene rings, unlikely to bind to metal atoms due to steric hindrance. This allows the two less hindered nitrogen atoms to face outwards to coordinate to metal atoms.

In complex **5.31** the copper atom is six-coordinate and lies on a crystallographic centre of inversion. Each copper atom coordinates to four separate pyrazine nitrogens through the least hindered nitrogen atom and two oxygen atoms from a perchlorate anion. Consequently, the overall coordination geometry of the copper atom is best described as pseudo-octahedral. The equatorial plane is occupied by the four pyrazine nitrogens from

separate ligands with Cu-N bond distances of 2.025Å and 2.042Å, and the two axial positions are occupied by the oxygen atoms from perchlorate anions with a Cu-O bond length of 2.542Å. This bond length between the copper atom and the oxygen atom of the perchlorate anion is similar to other structurally similar complexes in the literature.[294, 295] The axial bond lengths are significantly longer than the equatorial plane bond lengths which are indicative of Jahn-Teller distortion about the copper(II) metal atom. This type of octahedral coordination geometry with nitrogen heterocyclic ligands and two perchlorate anions about a copper(II) atom is not common as there are only seven structures listed in the *Crystallographic Structural Database* (Version 1.10, April 2008).

Each ligand has a V-shaped conformation, and is related to another co-bridging V-shaped ligand by a centre of inversion. Each ligand molecule is coordinated to two separate copper atoms acting as a bridge. The resulting complex is a double chain necklace-type one-dimensional polymer composed of M_2L_2 macrocyclic units that are linked together by copper atoms that act as spiro centers. Each spiro centre binds together two such macrocyclic units to propagate in one-dimension. A section of the one-dimensional necklace polymer chain is illustrated in figure 5.32 with the solvent molecules, perchlorate anions and hydrogens removed for clarity. The distance between copper atoms within a macrocycle is 14.693Å to give a reasonable sized cavity inside each macrocycle.

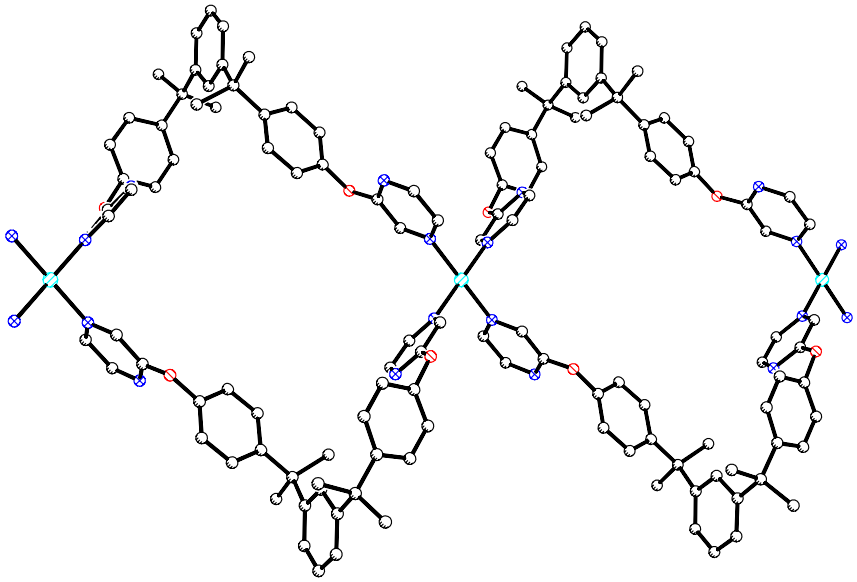


Figure 5.32 – *A section of the one-dimensional necklace polymer* ***5.31***.

In fact, each M_2L_2 macrocycle has a large enough cavity to have two acetone solvent molecules nestled within it. Both of these make short contacts to the aromatic rings of the ligand through the oxygen atom (2.681Å) and one of the methyl hydrogen atoms (2.726Å). Furthermore, the acetone molecules have short contacts with one another due to their close proximity within the cavity. In the extended structure the one-dimensional necklace polymer chains stack down the a-axis of the unit cell, with the distance between copper atoms in a stack of 9.321Å, which is the length of the a-axis. The necklace polymer chains are not interpenetrated due to the conformation of the bridging ligands, but interdigitated with only a few hydrogen bonding interactions between adjacent necklace chains. The perchlorate anions also make numerous short contacts with adjacent necklace chains.

The necklace topology of complex **5.31** is quite different to any previously reported complexes in this thesis. There have been many necklace-like complexes with big macrocyclic rings that are inter-linked by smaller bridging rings, usually copper motifs, that were made with the Bisphenol A and Bisphenol Z derived ligands discussed in chapter two. In comparison, there has only been one similar complex to **5.31** with the same necklace topology of M_2L_2 macrocycles linked together by a single metal atom. The other necklace-like complex with this type of topology was generated from the pyrazine substituted Bisphenol Z derived ligand with cobalt bromide (**2.66**). This complex **2.66** was composed of M_2L_2 macrocyclic units that were linked together by octahedral cobalt metal atoms.

*Crystal structure of the complex with $AgPF_6$ (**5.32**)*

Slow evaporation of a solution containing ligand **5.23** and silver hexafluorophosphate gave colourless plate-like crystals that were suitable for X-ray crystallography. The silver complex crystallises in the monoclinic space group $P2_1/m$ with half a ligand, two half-silver atoms, one hexafluorophosphate anion, one and a half acetone molecules and an ethanol solvate molecule in the asymmetric unit. A section of the coordination polymer is shown in figure 5.33 with the hydrogen atoms and uncoordinated solvent molecules excluded for clarity. The structure in figure 5.33 is grown about the crystallographic mirror plane in order to show the overall connectivity of the atoms in the extended structure.

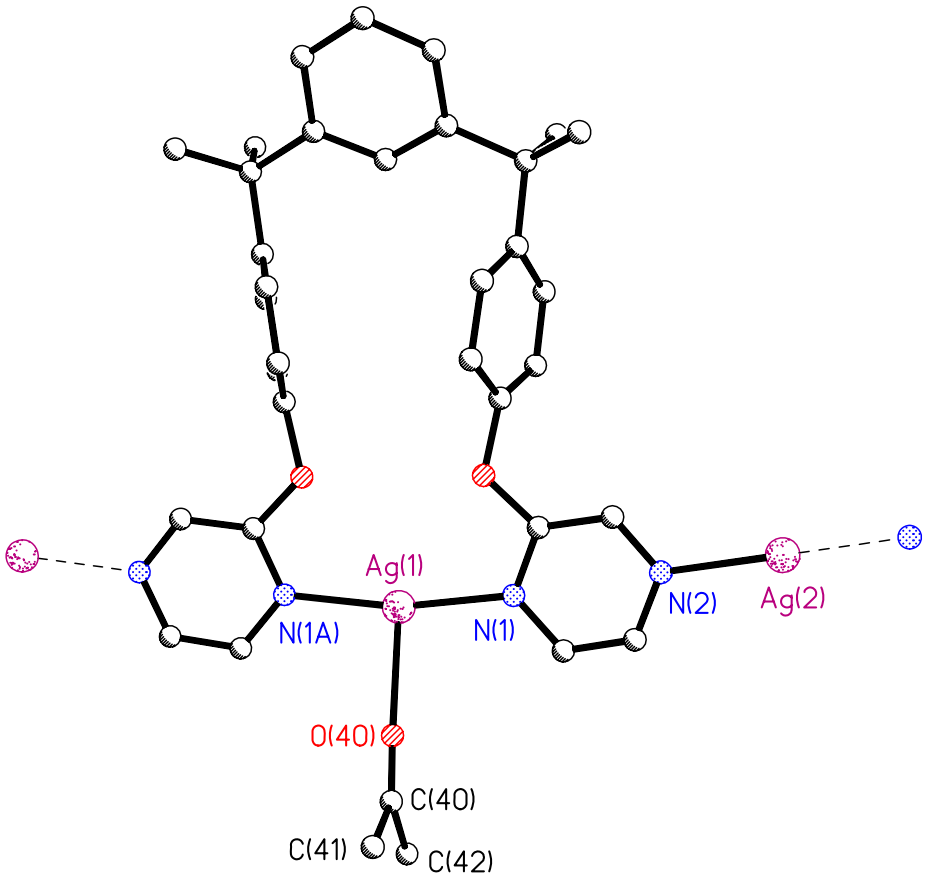


Figure 5.33 - *A section of the complex formed with ligand* ***5.23*** *and silver hexafluorophosphate. Selected bond lengths (Å) and angles (°): Ag1-N1 2.176(8), Ag2-N2 2.229(8), Ag1-O40 2.39(4), O40-C40 1.18(4), C40-C41 1.56(5), C40-C42 1.51(5), N1-Ag1-O40 95.2(2), O40-C40-C41 110.0(4), O40-C40-C42 135.0(5), C41-C40-C42 115.0(2), N1-Ag1-N1A 167.2(5).*

The adopted conformation of the ligand in complex **5.32** is completely different to that of the free ligand **5.23** in the solid state. Ligand **5.23** has more of a linear conformation in the solid state, in which it extends out the binding arms of the ligand thereby maximising the distance between nitrogen donor atoms. However, in complex **5.32** the ligand adopts a U-shaped conformation in order to chelate to the silver atom in a *trans* fashion, as shown in figure 5.33. The pyrazine rings of the ligand are almost perpendicular to the attached benzene rings and coplanar with each other in complex **5.32**. The two internal nitrogen atoms that are chelated to the Ag1 atom are oriented to point inwards, whereas the external nitrogen atoms are facing outwards to coordinate to another silver atom (Ag2).

The Ag1 atom lies on a mirror plane and the Ag2 atom lies on a centre of inversion. The Ag1 atom is chelated to two internal pyrazine nitrogen atoms from the same ligand in a trans-spanning arrangement to give a 20-membered chelate ring. The Ag1 atom is also coordinated to an acetone molecule to give the silver atom a 'T-shaped' geometry with a N-Ag-N bond angle of 167.2°. The bond distance between the silver atom and the coordinated oxygen atom from the acetone solvent molecule is 2.39Å. There is no indication of any bonding interactions between the Ag1 atom and the ether oxygen atoms of the chelating ligand, with a large Ag-O distance of 2.967Å. The Ag2 atom, which lies on a crystallographic centre of inversion, is coordinated to the external nitrogen atoms of the ligand with a linear geometry of 180°. Consequently, each ligand is chelated to an Ag1 atom to form a chelate ring through the internal nitrogen atoms and then bridges to another silver atom through the other external nitrogens atoms of the pyrazine. The resulting complex is a fascinating chain of chelate rings in which the ligand coordinates through internal nitrogen atoms and the external nitrogens bridge into a chain. The silver chelate rings alternate from one side to the opposite side of the chain along the b-axis. A section of the silver polymer chain is shown in figure 5.34 below. The Ag-N distances for the internal bonds in the 20-membered chelating ring are 2.176Å, while the Ag-N bond distance through the external nitrogen atoms of the pyrazine that link into the external chain is slightly longer at 2.229Å.

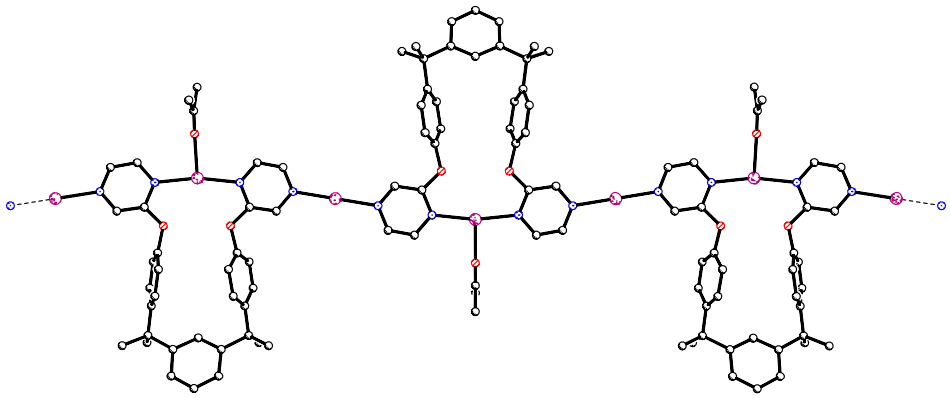


Figure 5.34 – *Perspective view of the silver complex chain of* ***5.32****, illustrating the coordination of silver atoms through both nitrogens of the pyrazine rings and the alternation of the chelate rings from one side to another along the chain.*

It is advantageous for chemists to design and construct ligands that have heterocycles with multiple binding domains. Pyrazine is one such heterocycle that has the ability to potentially bridge two metal atoms in order to generate more interesting and complex structures. Supramolecular structures that have coordination through both nitrogen atoms of the pyrazine heterocycle to silver(I) have been explored in some detail.[130]

The silver polymer chains pack into sheets through C-H···Ag bonds between silver atoms and a hydrogen atom of the central phenylene ring spacer unit from another polymer chain (2.683Å). The non-coordinating hexafluorophosphate anions and non-coordinated acetone and ethanol solvent molecules fill in voids in the crystal lattice and link together the sheets through various short contacts.

Attempts were made to crystallise other similar silver complexes with ligand **5.23**. Another silver polymer chain complex was obtained with silver perchlorate (**5.33**), which crystallised in the monoclinic space group $P2_1/n$ with four times the contents in the asymmetric unit. This silver perchlorate complex (**5.33**) had a very similar overall topology to complex **5.32**. Furthermore, the silver perchlorate complex analysed as a M_2L compound, which is the same stoichiometry as the silver hexafluorophosphate complex **5.32**.

*Other complexes with ligand **5.23***

Ligand **5.23** was reacted with a variety of metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $Pd(PhCN)_2Cl_2$, $ZnCl_2$ and $ZnBr_2$ under a variety of different conditions. Three of these metal salts upon complexation gave X-ray quality crystals with the pyrazine substituted ligand **5.23**, which have been discussed in some detail above. Regrettably, crystals suitable for X-ray crystallography were not formed with all the metal salts. Most of the complexes that formed gave either precipitates immediately or crystalline solids that were unable to be recrystallised. Sometimes instead of complexation, X-ray quality crystals were grown of either the ligand itself or the starting metal salt directly.

Complexation of ligand **5.23** with copper salts $CuCl_2$ and CuI gave crystalline solids that analysed as M_2L compounds. This stoichiometry is the same as the elemental analysis of the copper perchlorate complex **5.31**, which generated a necklace polymer. One can therefore assume that a polymeric structure with a similar topology to **5.31** was also generated with $CuCl_2$ and CuI. Throughout this thesis the majority of the necklace-type polymers formed were made with the copper metal salts $CuCl_2$ and CuI. All of these necklace polymers are composed of M_2L_2 macrocycles linked by copper square motifs. Reaction of ligand **5.23** with $Pd(PhCN)_2Cl_2$ gave a yellow precipitate immediately that also analysed as a M_2L compound with one water molecule.

A yellow precipitate formed immediately upon complexation of ligand **5.23** with $PdCl_2$, which was unable to be recrystallised. Analysis of this precipitate revealed a M:L compound with no solvent molecules.

Complexes with ligand 5.24

*Crystal structure of the complex with $CuCl_2$ (**5.34**)*

Beautiful blue crystal plates of complex **5.34** were produced from the quinoline substituted ligand **5.24** and copper chloride in a methanol:dichloromethane solution. The copper chloride complex **5.34** crystallises in the monoclinic space group $P2_1/c$ as a discrete monomeric complex. The asymmetric unit contains one whole ligand molecule, one copper atom, two chlorine atoms and two methanol solvate molecules each of half occupancy. A perspective view of the asymmetric unit is shown in figure 5.35 in which the hydrogen atoms and solvent molecules have been excluded for clarity.

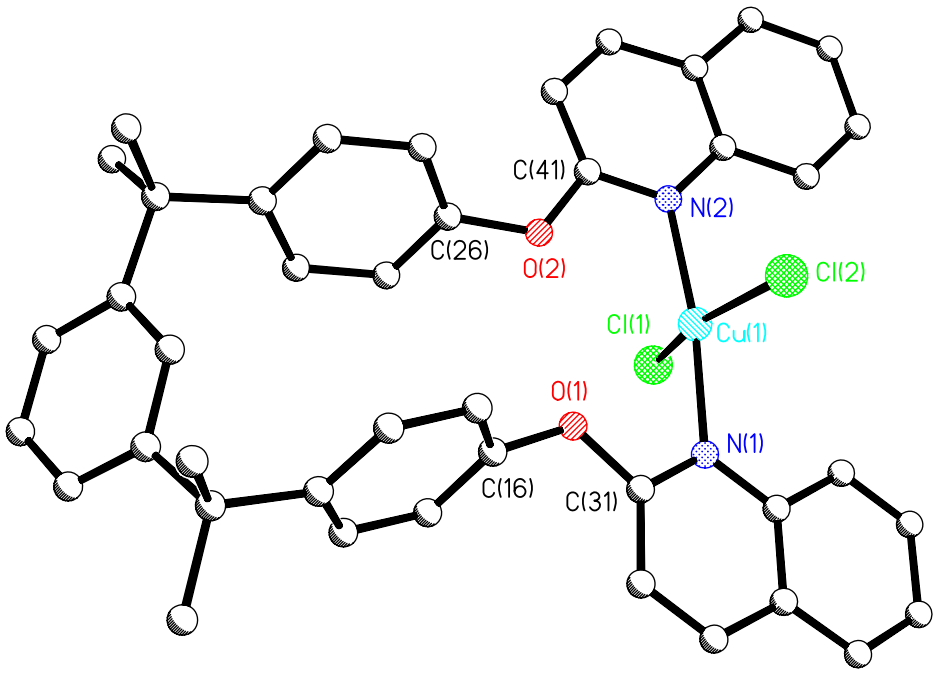


Figure 5.35 – *View of the discrete 20-membered chelate ring in complex* ***5.34****. Selected bond lengths (Å) and angles (°): Cu1-N1 2.016(3), Cu1-N2 2.010(3), Cu1-Cl1 2.2338(9), Cu1-Cl2 2.2531(9), C16-O1 1.406(4), O1-C31 1.353(4), C31-N1 1.311(4), C26-O2 1.407(4), O2-C41 1.354(4), C41-N2 1.311(4), N2-Cu1-N1 172.1(1), N2-Cu1-Cl1 88.88(8), N1-Cu1-Cl1 91.08(8), N2-Cu1-Cl2 91.32(8), N1-Cu1-Cl2 91.19(8), Cl1-Cu1-Cl2 161.68(4), C31-O1-C16 119.9(3), N1-C31-O1 112.2(3), C41-O2-C26 121.6(2), N2-C41-O2 111.6(3).*

Once again the ligand in complex **5.34** adopts a completely different conformation to that of ligand **5.24** itself in the solid state. Ligand **5.24** adopted an unusual hook-shaped conformation in the solid state in which the ligand twists around so that one of the nitrogen atoms is nestled inside a cavity of its own. Interestingly, the quinoline substituted ligand in complex **5.34** adopts a U-shaped conformation on coordination to the copper atom, with the central phenylene spacer group directly opposite the copper atom in the complex acting as the bottom part of the U-shape. Each of the aromatic quinoline rings is almost perpendicular to the attached benzene rings with the two nitrogen donor atoms orientated to point inwards in order to chelate to the metal atom. The two benzene rings that flank each side of the phenylene spacer group are in one plane and the two quinoline rings are in another. The quinoline rings are almost coplanar, with their mean planes tilted by approximately 11° to one another as a result of the conformation of the ligand in complex **5.34**. This can be more clearly seen in a

space-filling diagram of complex **5.34** in figure 5.36, which shows the two almost coplanar quinoline rings and the small cavity inside the ring.

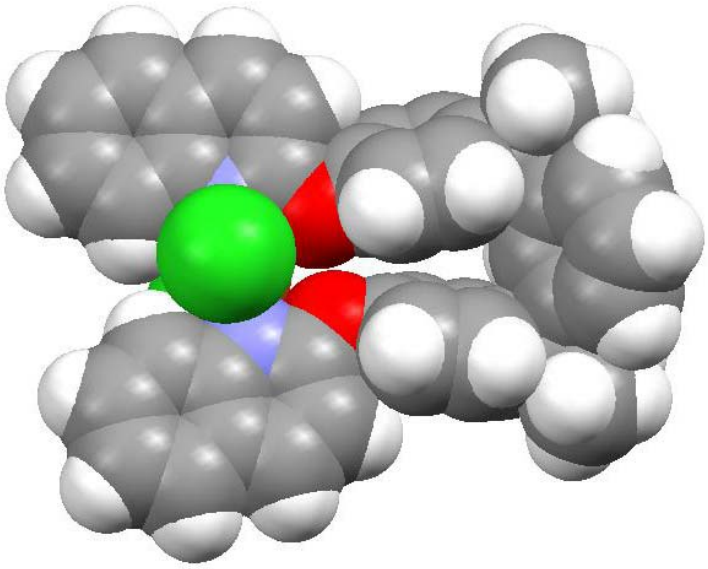


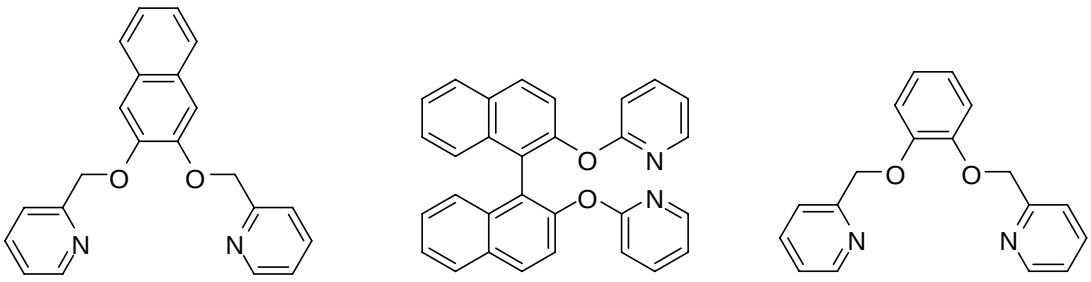
Figure 5.36 – *Space-filling diagram of complex* ***5.34*** *illustrating the almost coplanar quinoline rings.*

The resulting complex is a large discrete 20-membered copper chelate ring. The copper atom is 4-coordinate chelating to two quinoline nitrogen atoms of the same ligand and two chlorine atoms with a distorted square planar coordination geometry, as a result of the copper atom just sitting out of the coordination plane of the chlorine and nitrogen atoms. The ligand chelates to the copper atom in a trans-spanning arrangement. There is no indication of any bonding interactions between the copper atom and the oxygen atoms of the chelating ligand, with Cu-O distances of 2.719Å and 2.816Å, which are too long to be considered as a real bond. The Cu-N bond lengths are 2.016Å and 2.010Å, and the Cu-Cl bond lengths are 2.2338Å and 2.2531Å, both of which are within the normal ranges of other copper chloride complexes in this thesis. The angles between the two benzene rings that flank each side of the central benzene ring are 74.52° and 84.38°, while the angle between the mean planes of the two flanking benzene rings is 21.75°. The two flanking benzene rings are orientated to face each other as a result of the conformation of the ligand and are separated by a distance of 4.271Å, which is far too long for π-π stacking interactions to occur between the rings.

The internal cavity is not large enough to play host to any guest molecules and the acetone solvent molecules lie outside the copper chelate ring.

In the packing structure the copper chloride chelate rings arrange with numerous interactions between mononuclear units within the extended crystal lattice. There are C-H···Cl interactions between the chlorine atoms and both aromatic and methyl hydrogen atoms of the ligand that lie in the range of 2.773Å-2.946Å. The acetone solvent molecules also interact extensively with the chelate rings through hydrogen bonds and other short contacts to fill voids in the crystal lattice.

It appears that the conformation of the ligand in complex **5.34** has arranged itself especially into a U-shaped conformation with its quinoline rings almost coplanar to one another, in order to allow the nitrogen donor atoms to chelate to the copper atom. The overall result is a large 20-membered chelate ring. This is not the only example of such a chelate ring and a few examples of other large chelate rings have been generated by past members of the Steel group. O'Keefe et al. synthesised and designed ligands based around naphthalene and binaphthalene cores and then investigated their coordination chemistry.[118] The two ligands, (**a**) and (**b**) shown in figure 5.37 are two examples of ligands that generated chelate rings on reaction with metal salts. Both of these ligands formed 11-membered chelate rings. Interestingly, O'Keefe et al. found that the naphthalene ligand **(a)** acted as a tetradentate ligand with silver nitrate by chelating through both the oxygen atoms and the two pyridine donor atoms of the ligand.[118] In contrast, with copper chloride ligand **(a)** only coordinated through the two pyridine nitrogen atoms in a bidentate manner. O'Keefe et al. also generated 11-membered chelate rings with palladium chloride and copper chloride with ligand **(b)**, both of which were bidentate with coordination through the two nitrogen donor atoms only. Not long after, Fitchett et al. generated a couple of 11-membered chelate rings with the catechol based ligand **(c)**, illustrated in figure 5.37.[107] Fitchett et al. found that ligand **(c)** acted as a tetradentate ligand with copper chloride by coordinating through both the oxygen and pyridine donor atoms, and as a bidentate ligand with silver nitrate by coordinating through just the nitrogen atoms.



(a) **(b)** **(c)**

Figure 5.37 – *Other ligands that have formed large chelate rings with various metal salts.* ***(a)*** *2,3-Bis(2-pyridylmethoxy)naphthalene,* ***(b)*** *(±)-2,2'-bis(2-pyridyloxy)-1,1'-binaphthalene,* ***(c)*** *1,2-bis(2-pyridylmethoxy)benzene.*

Consequently, it was hoped that the Bisphenol M derived ligand **5.24** would coordinate to metal atoms through both the oxygen and pyridine donor atoms in a unique tetradentate chelating fashion, similar to that achieved by O'Keefe and Fitchett. Therefore ligand **5.24** was reacted with a variety of silver salts.

*Crystal structure of the complex with $AgClO_4$ (**5.35**)*

Another discrete 20-membered chelate ring was made from ligand **5.24** and silver perchlorate. This complex was very similar to the copper chelate ring **5.34**, with a similar arrangement of atoms in the chelate ring, but different counterions and solvent molecules. The silver perchlorate complex **5.35** crystallises in the same monoclinic space group $P2_1/c$. The asymmetric unit contains one whole ligand molecule, one silver atom, one perchlorate counterion and two chloroform solvent molecules, as shown in figure 5.38 in which the hydrogen atoms and solvent molecules have been excluded for clarity. The perchlorate anion is not coordinated.

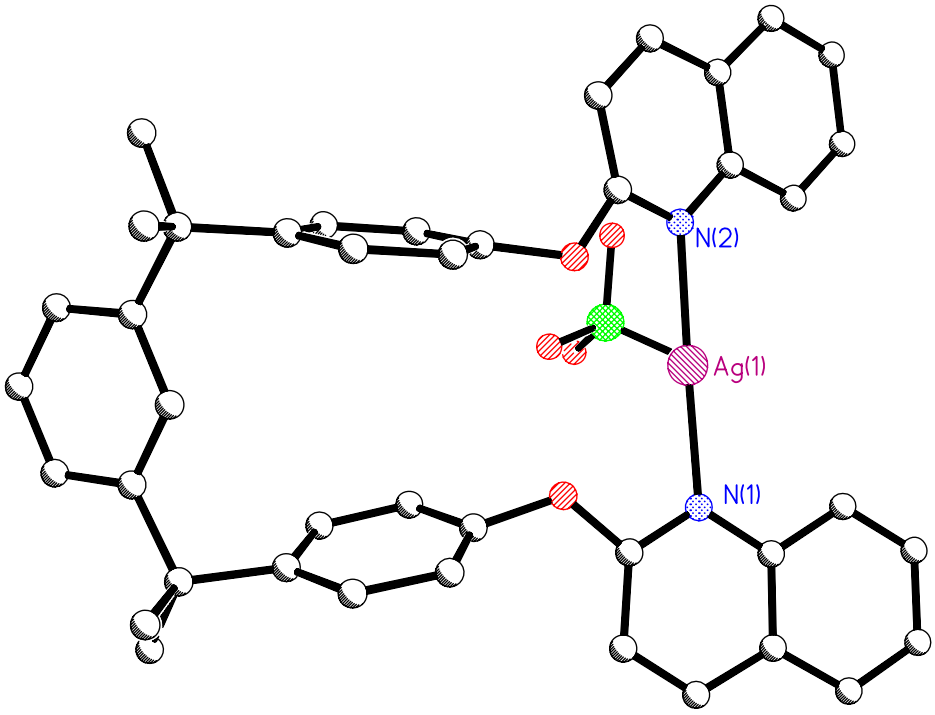


Figure 5.38 – *View of the discrete 20-membered chelate ring* ***5.35****. Selected bond lengths (Å) and angles (°): Ag1-N1 2.135(2), Ag1-N2 2.144(2), N1-Ag1-N2 171.57(6).*

In complex **5.35** the quinoline substituted ligand adopts the same U-shaped conformation to complex **5.34**, with the bottom part of the U-shape formed by the central phenylene spacer unit. The two quinoline rings are in the same orientation, perpendicular to the attached benzene rings with the nitrogens facing inwards to chelate to the silver atom. Once again the two benzene rings that flank each side of the phenylene spacer group are parallel. The two quinoline rings are almost coplanar to each other with their mean planes tilted by approximately 18.9° to one another. This deviation from coplanarity of the quinoline rings is much larger than that of 11° observed with the copper complex **5.34**.

The ligand chelates to the silver atom to form the same 20-membered ring as complex **5.34**. As a result there are a lot of similarities between the two complexes. Firstly, the silver chelates to the quinoline nitrogen donors with an almost linear geometry and a bond angle of 171.57° and the Cu-N bond lengths both lie within the normal ranges. The distance between the silver atom and the two oxygen atoms of the ligand are 2.799Å and 2.867Å, which is far too long to be considered as a bond. The angles between the three benzene rings of the ligand that help to form the U-shaped

conformation are also very similar. The angles between the two benzene rings that flank the central benzene ring are 73.40° and 89.86°, which are very similar to those in the copper chloride complex. However, the angle between the mean planes of the flanking benzene rings in complex **5.35** is slightly less at 16.84°. Once again the two flanking benzene rings are facing each other in such a way that is ideal for π-π stacking inside the chelate ring; however the distance between the two rings of 4.453Å is too long for π-π stacking to occur. Both the copper chloride complex **5.34** and silver perchlorate complex **5.35** adopt the same U-shaped conformation by chelating to a metal atom in a bidentate way.

In the extended structure the silver chelate rings closely pack with extensive hydrogen bonding interactions and short contacts between chelate rings, perchlorate anions and chloroform solvent molecules throughout the crystal lattice. The perchlorate anions interact extensively with both aromatic and non-aromatic hydrogen atoms from the ligand with distances that lie in the range between 2.572-2.717Å. The perchlorate anions also make short contacts with the chloroform solvent molecules. There are also some C-H···Cl interactions between chloroform solvent molecules and ligand units.

*Crystal structure of the complex with $AgPF_6$ (**5.36**)*

Ligand **5.24** was dissolved in chloroform and silver hexafluorophosphate was dissolved in acetone. The solutions were combined to give a colourless solution, which yielded nice colourless block-like crystals on slow evaporation that were suitable for X-ray crystallography. Subsequent X-ray analysis revealed yet another discrete 20-membered chelate ring similar to the previous two complexes **5.34** and **5.35**. The complex solved in the same monoclinic space group $P2_1/c$ as **5.34** and **5.35**, with the same cell constants as the silver perchlorate complex **5.35**. Thus the silver hexafluorophosphate complex **5.36** is isomorphous with **5.35**. Consequently, complex **5.36** is also isostructural with the other silver perchlorate complex **5.35**, because it has the same cell constants and positioning of atoms. Complex **5.36** contains one whole ligand molecule, one silver atom, one disordered $PO_2F_2^-$ counterion and two chloroform solvent molecules in the asymmetric unit, as shown in figure 5.39. A slightly different orientation of the chelate

ring is shown in figure 5.39 for variety and excluded from the diagram are the hydrogen atoms and solvent molecules.

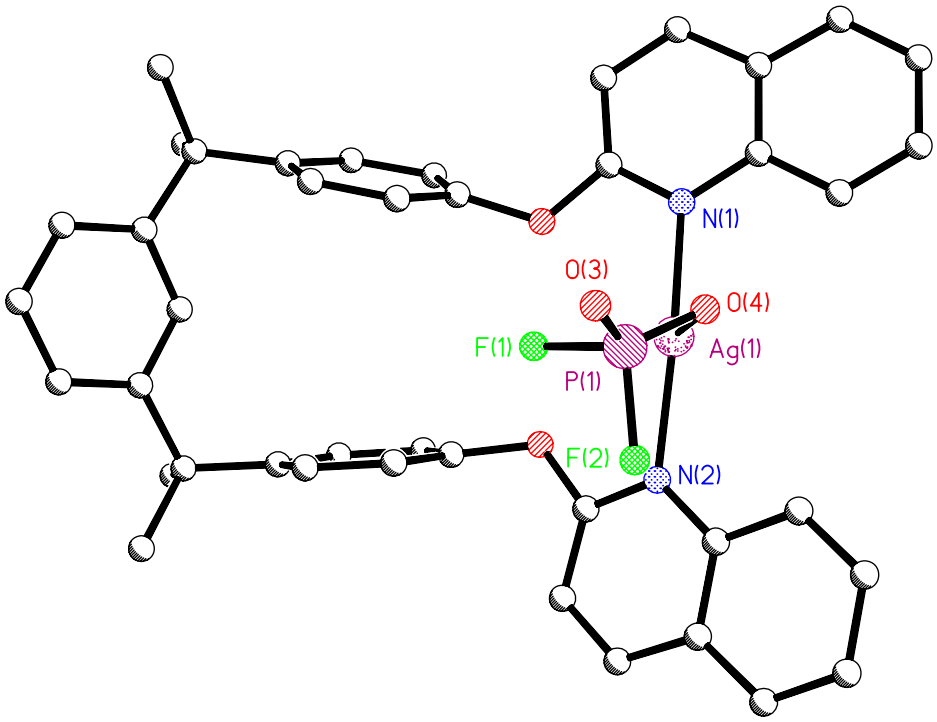


Figure 5.39 - *View of the discrete 20-membered chelate ring in complex* ***5.36*** *with silver hexafluorophosphate. The minor 10% component of the disordered $PO_2F_2^-$ group is not shown. Selected bond lengths (Å) and angles (°): Ag1-N1 2.153(2), Ag1-N2 2.164(2), Ag1-O4 2.597(5), P1-O3 1.465(2), P1-F2 1.553(1), P1-F1 1.572(2), N1-Ag1-N2 167.35(6), N1-Ag1-O4 97.67(7), N2-Ag1-O4 94.92(7), O3-P1-O4 123.9(2), O3-P1-F2 108.95(9), O4-P1-F2 109.0(1), O3-P1-F1 107.6(1), O4-P1-F1 107.4(1), F2-P1-F1 96.5(1), P1-O4-Ag1 111.9(2).*

In the reaction, the octahedral hexafluorophosphate anion decomposes to a tetrahedral $PO_2F_2^-$ anion, which in this case coordinates to the silver atom through an oxygen atom, as depicted in figure 5.39. The $PO_2F_2^-$ anion is quite a common decomposition product of the hexafluorophosphate anion and there have been many complexes characterised with this anion in the literature. In fact a search on the *Crystallographic Structural Database* (Version 1.10, April 2008) revealed thirty-eight complexes that contain the tetrahedral $PO_2F_2^-$ anion somewhere in the crystal structure, sixteen of which are coordinated to a metal atom. In complex **5.36** the silver atom interacts weakly with the $PO_2F_2^-$ anion with an Ag-O bond length of 2.597Å, which is similar to the bond lengths of other silver coordination complexes of this anion.[296, 297] In addition the $PO_2F_2^-$ anion

also has some disorder of a couple of the atoms. One of the fluorine atoms and one of the oxygen atoms are disordered over two sites, with the two major contributing atoms occupied 90% of the time.

Once again the two nitrogen donor atoms chelate to the silver atom with a distorted linear geometry of 167.35°. The small deviation from linearity between the two nitrogen atoms and the silver atom is due to a slight pyramidalisation of the silver atom, because of the coordination to the $PO_2F_2^-$ anion. As complex **5.36** is similar to the other two complexes it adopts exactly the same U-shaped conformation of the ligand in order to chelate to the metal atom. This includes the orientation of the aromatic rings, which are once again almost perpendicular to one another and the corresponding angles between the two benzene rings that flank each side of the central benzene ring. Once again the ligand is bidentate, as it only chelates through the nitrogen donor atoms of the ligand.

In the packing structure the chelate rings pack with hydrogen bonding interactions and other short contacts between the coordinated $PO_2F_2^-$ anion, chloroform solvent molecules and atoms from the main structure. There are also some edge-to-face and C-H···π interactions between mononuclear units in the extended structure as well as π-π stacking between adjacent quinoline rings (3.642Å).

Another discrete 20-membered chelate ring was obtained with silver tetrafluoroborate (**5.37**), which had the same overall topology as the other three chelate rings. It crystallised in the triclinic space group P-1 with twice the contents in the asymmetric unit. The compound analysed as a 1:1 complex.

*Other complexes with ligand **5.24***

Ligand **5.24** was reacted with a variety of metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $Pd(PhCN)_2Cl_2$, $ZnCl_2$ and $ZnBr_2$. Crystals suitable for X-ray analysis were grown of five of these, all of which were characterised by X-ray crystallography as discrete 20-memebered chelate rings and all analysed as 1:1 complexes.

Reaction of ligand **5.24** with $PdCl_2$ produced a fine orange crystalline solid that was too small for X-ray crystallography. The compound analysed with a 1:1 ratio. This ratio suggests the possible formation of another discrete 20-membered chelate ring similar to those already characterised.

Complexation of ligand **5.24** with another palladium salt, $Pd(PhCN)_2Cl_2$, produced huge clusters of orange block-like crystals within a day of standing. These crystals were much larger than the fine crystal plates obtained with $PdCl_2$ and were therefore put up for X-ray. Unfortunately, the crystals were highly twinned and the structure was unable to be solved despite several attempts. Once again the orange crystals analysed as a 1:1 complex, which suggests the formation of another discrete 20-membered chelate ring.

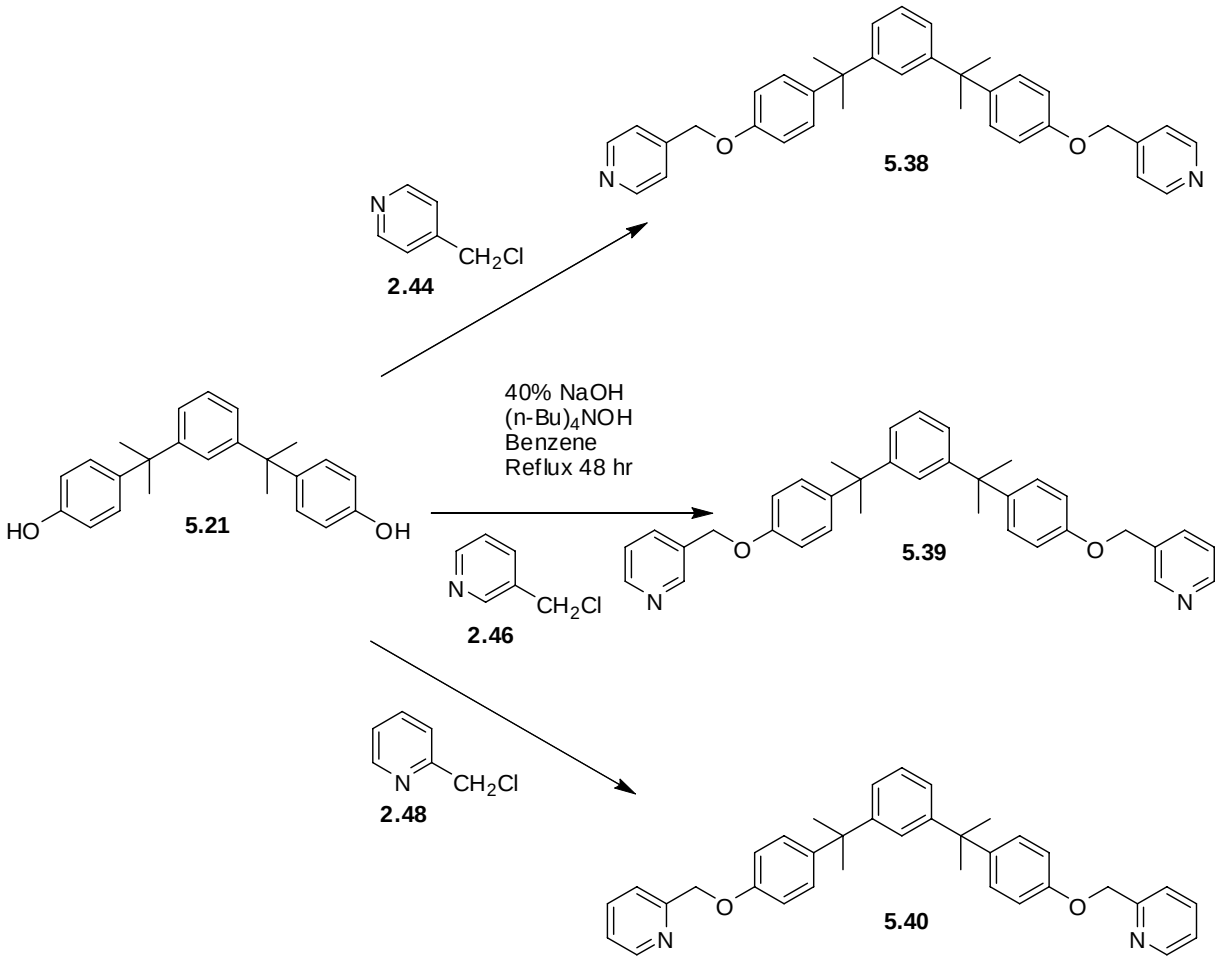
Complexes with ligand 5.25

The Bisphenol M derived ligand **5.25** was reacted with a variety of metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $Pd(PhCN)_2Cl_2$, $ZnCl_2$ and $ZnBr_2$ under a variety of conditions. Regrettably, no crystals suitable for X-ray crystallography were obtained with any of these metal salts. Most of the complexes that formed gave either precipitates immediately or crystalline solids that were unable to be recrystallised. Sometimes instead of complexation, crystals were grown of either the free ligand or starting metal salt. This was how the ligand **5.25** was able to be fully characterised.

Elemental analyses were carried out on the yellow precipitates obtained with the palladium metal salts $PdCl_2$ and $Pd(PhCN)_2Cl_2$. Both of the precipitates analysed with 1:1 ratios. It seems reasonable to assume that discrete complexes have formed with the quinoxaline substituted ligand **5.25**, similar to the 20-membered chelate rings generated with the quinoline substituted ligand **5.24**. Reaction of ligand **5.25** with CuI gave a yellow solid that also analysed with a 1:1 ratio.

Synthesis of the Bisphenol M based -CH_2O- spaced ligands

Finally, three more ligands were synthesised from the Bisphenol M core with a spacer group containing two atoms, instead of just one in order to complete the set of Bisphenol M derived ligands. The two atom spacer group is composed of a methyleneoxy group that is positioned between the benzene ring and a 2-, 3- or 4-substituted pyridine ring. The addition of such a two atom spacer group is expected to add more flexibility to the ligand structure and along with the phenylene spacer group generate more intricate complexes.



Scheme 5.6 – *Synthesis of new ligands **5.38**, **5.39** and **5.40** derived from the Bisphenol M core.*

Once again the three methyleneoxy spacer group ligands based around the Bisphenol M backbone were synthesised via a phase-transfer-catalysed (PTC) alkylation reaction,[102, 172] as shown in Scheme 5.6. The double alkylation of Bisphenol M with three isomeric

chloromethylpyridines gave crude ligands **5.38**, **5.39** and **5.40** that were then recrystallised from petroleum ether/ethyl acetate. Brown solids were isolated of ligands **5.38** and **5.39** in good yields of 98% and 90%, respectively. Ligand **5.40** was also isolated as a crystalline solid in a good yield of 84%.[113] All three ligands were then fully characterised by elemental analyses, mass spectrometry, melting points and ^{1}H NMR and ^{13}C NMR spectroscopy.

Complexes with ligand 5.38

*Crystal structure of the complex with $AgPF_6$ (**5.41**)*

Ligand **5.38** was dissolved in chloroform and layered upon a solution of silver hexafluorophosphate dissolved in acetone. Slow evaporation and vapour diffusion of ethyl acetate into the resulting colourless solution gave clumps of colourless block-like crystals on the bottom of the vial that were perfect for X-ray crystallography. After only a day the reaction mixture had gone a brown colour as well, due to the deposition of metallic silver. The structure solved in the monoclinic space group $P2_1/c$. The asymmetric unit contains one whole ligand molecule, one silver atom, one hexafluorophosphate anion, one acetone solvent molecule and a chloroform solvent molecule, both of partial occupancy. Two of these asymmetric units combine about a crystallographic centre of inversion that lies between the two silver atoms to give a dimetallic macrocycle, as shown in figure 5.40 with the hydrogen atoms and solvent molecules omitted for clarity.

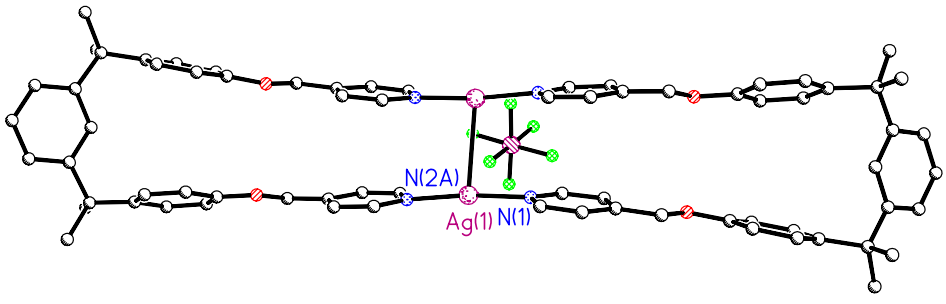


Figure 5.40 – *Perspective view of the discrete dimetallic silver macrocycle* ***5.41****. Selected bond lengths (Å) and angles (°): Ag1-N1 2.124(3), Ag1-N2A 2.141(3), Ag1-Ag1A 3.1586(7), N1-Ag1-N2A 174.2(1), N1-Ag1-Ag1A 89.96(9), N2A-Ag1-Ag1A 95.86(9).*

The ligand adopts a U-shaped conformation in complex **5.41**, with the bottom part of the U-shape formed by the central benzene spacer unit. The two benzene rings that flank the central benzene ring are almost perpendicular to the central benzene ring with angles between the rings mean planes of approximately 78.70° and 80.95°, while the angle between the mean planes of the two flanking benzene rings is 20.47°. The pyridine binding arms of the ligand adopt are extended out in an *anti* conformation with the pyridine rings almost coplanar to the attached benzene rings and the nitrogen donor atoms pointing outwards. The co-planarity of the U-shaped binding arms is also reflected in the methyleneoxy spacer group adopting an *anti*-periplanar type arrangement, with C-C-O-C torsional angles of 174.9° and 175.3°.

The resulting structure is a discrete macrocycle composed of two U-shaped ligand molecules and two silver atoms that combine about a centre of inversion to give a large dimetallic macrocycle. Each of the U-shaped units is a 27-membered macrocycle that combines with another to give a much larger 52-membered dimetallic macrocycle. The complex could also be classified as a [2+2] macrocycle, which has a remarkable ten aromatic rings in the structure, six of which are benzene rings and four of which are pyridine rings. The silver atoms coordinate to the nitrogen donors with an almost linear geometry and the Ag-N bond lengths of 2.124Å and 2.141Å both lie within the normal range. If one considers the silver-silver bond to be real the silver atoms adopt a T-shaped geometry.

The U-shaped conformation of the ligand in complex **5.41** is ideal for the formation of a symmetrical macrocycle. The macrocycle has a rectangular shape in which the short sides of the rectangle are made up of the two central benzene spacer units of each ligand and the corners are defined by the propyl groups. The distance between the two central benzene spacer units across the length of the rectangle is 27.614Å, which to the best of our knowledge is the longest known macrocycle of this sort. The height of the rectangle varies along the length of the macrocycle as a consequence of the conformation of the ligand and therefore there is no exact distance to quote.

There has been much debate over the years as to what distance between silver atoms is considered as a real silver-silver bonding interaction.[298-304] The distance between the silver(I) atoms in complex **5.41** is 3.159Å, which is a little shorter than the sum of the van der Waals radii of two silver(I) atoms (3.44Å).[184, 303] Conversely the bond distance

is longer than the distance between two atoms in metallic silver (2.89Å),[298, 299, 301-303] which therefore suggests a weak silver-silver bond if any. In general, non-bridging complexes with silver-silver bonding interactions have bond lengths that lie within the range of 2.8-3.3Å.[301] The literature also indicates that in general the majority of silver-silver bonding interactions lie within the ranges of 2.740-3.085Å.[302] A distance between silver atoms longer than 3.3Å is considered unlikely to be a real silver intermetallic bond. Hence there is continuous and ongoing debate in the literature as to what constitutes a real silver-silver bond distance. Despite this the literature does suggest that there is at the very least a partial silver bonding interaction in complex **5.41**.

As a consequence of the U-shaped conformation of the ligand and the orientation of the aromatic groups the benzene rings and pyridine rings in the macrocycle are nearly aligned parallel with one another, which is ideal for π-π stacking to occur between rings within a macrocycle. Consequently, pyridine rings π-π stack with one another with a favorable distance of 3.543Å. However, the distance between the benzene rings within a macrocycle is 4.385Å, which is too great for π-π stacking interactions to occur.

*Crystal structure of the complex with $AgClO_4$ (**5.42**)*

Another 52-membered silver dimetallic macrocycle was prepared from ligand **5.38** and silver perchlorate under the same conditions as complex **5.41**. These colourless block-like crystals, which were suitable for X-ray crystallography, solved in the same space group and had the same cell constants as **5.41**. In fact the structure is isomorphous but not quite isostructural to the complex **5.41**, with a similar arrangement of atoms but a different counterion. Complex **5.42** contains one whole ligand molecule, one silver atom, one perchlorate anion, which is partially disordered and a chloroform solvent molecule. The silver atom is disordered over two sites with the major contributing silver atom occupied 77% of the time and the minor contributing silver atom occupied only 23% of the time. The perchlorate anion is rotationally disordered about three of the oxygen atoms. A perspective view of the silver dimetallic macrocycle from a different orientation is depicted in figure 5.41, with the hydrogens and chloroform solvent molecule excluded for clarity.

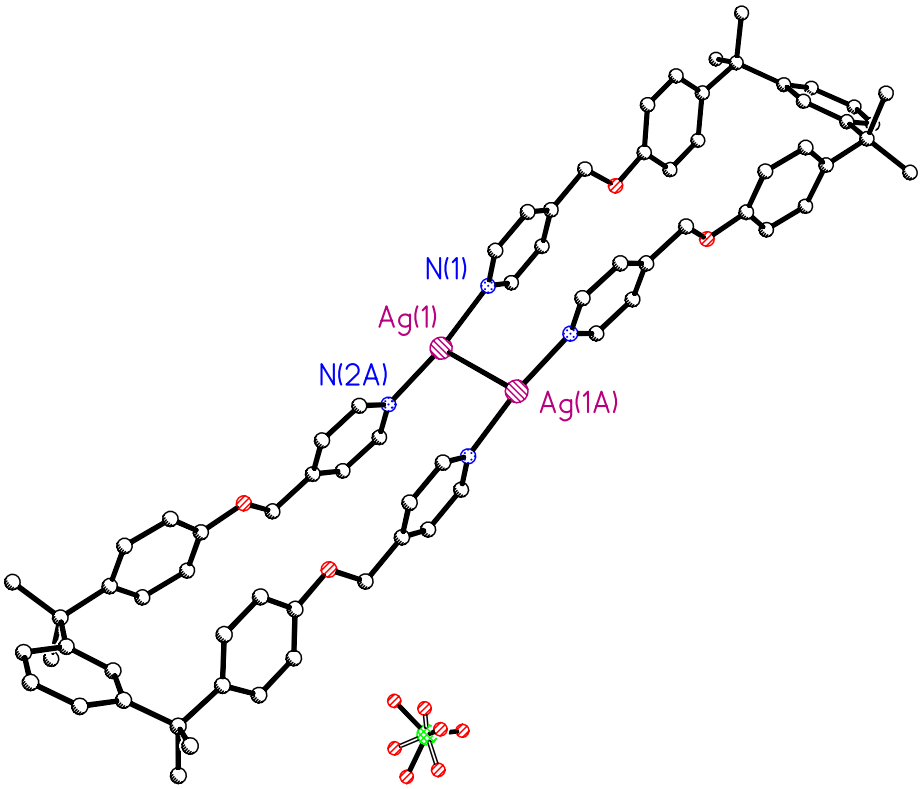


Figure 5.41 - *Perspective view of the discrete dimetallic silver macrocycle* ***5.42****. Selected bond lengths (Å) and angles (°): Ag1-N1 2.164(6), Ag1-N2A 2.111(6), Ag1-Ag1A 3.157(4), N2A-Ag-N1 173.7(2), N2A-Ag1-Ag1A 95.3(2), N1-Ag1-Ag1A 90.1(2).*

In complex **5.43** the ligand adopts the same U-shaped conformation as complex **5.41**, with the bottom part of the U-shape formed by the central phenylene spacer unit. In addition the two phenylene spacer units are each slightly tilted in opposite directions from one another, which is clearly seen in figure 5.41. The two flanking benzene rings of each ligand are once again perpendicular to the central benzene ring at the centre of the U-shape with angles between the central benzene ring and each of the two flanking benzene rings of 75.02° and 82.34°, which are similar to angles seen in **5.41**. The angle between the mean planes of the two flanking benzene rings is 22.76°, which is slightly more of an angle than in **5.41**. Once again, the binding arms of the ligand and the sides of the U-shape adopt the same *anti*-periplanar arrangement about the methyleneoxy group with C-C-O-C torsional angles of 170.5° and 175.1°.

The two U-shaped ligands and two silver atoms combine about a centre of inversion to give a silver dimetallic rectangular macrocycle that is isomorphous to **5.41**. Once again

the silver atom coordinates to the nitrogen atoms with a linear geometry and has similar Ag-N bond lengths to complex **5.41**. The distance between the two central benzene spacer units across the length of the rectangle is 27.446Å, which is slightly shorter than in **5.41**. The distance between silver atoms is 3.157Å, which is almost identical to the intermetallic silver-silver distance observed in complex **5.41** and is considered reasonably weak.

Once again there are π-π stacking interactions between the pyridine rings within a macrocycle due to the conformation and overall orientation of the ligand in the macrocycle. The two pyridine rings of the same ligand align parallel to one another and π-π stack with a distance of 3.535Å. The benzene rings of the same ligand also align with a distance that is too long for π-π stacking interactions to occur (4.354Å).

*Crystal structure of the complex with $AgCF_3SO_3$ (**5.43**)*

Colourless block-like crystals of yet another dimetallic silver macrocycle were prepared from ligand **5.38** with a different silver salt, silver trifluoromethanesulfonate. Exactly the same solvents and conditions to complexes **5.41** and **5.42** were adopted and the structure solved in the same space group as **5.41** and **5.42** with similar cell constants. The silver trifluoromethanesulfonate complex **5.43** has one ligand molecule, one silver atom, one trifluoromethanesulfonate anion and a chloroform solvent molecule in the asymmetric unit. A side on view depicting the silver dimetallic macrocycle is shown in figure 5.42 for variety, with the hydrogens and chloroform solvent molecule excluded for clarity. There is some minor disorder in the position of the silver atom and there is also a little disorder in the position of the sulfur atom in the trifluoromethanesulfonate anion, which is disordered over two sites. As a consequence of this disorder the structure refined poorly, giving a final R_1 value of 8.25%. Despite this the structure was able to be proven unambiguously and fully described.

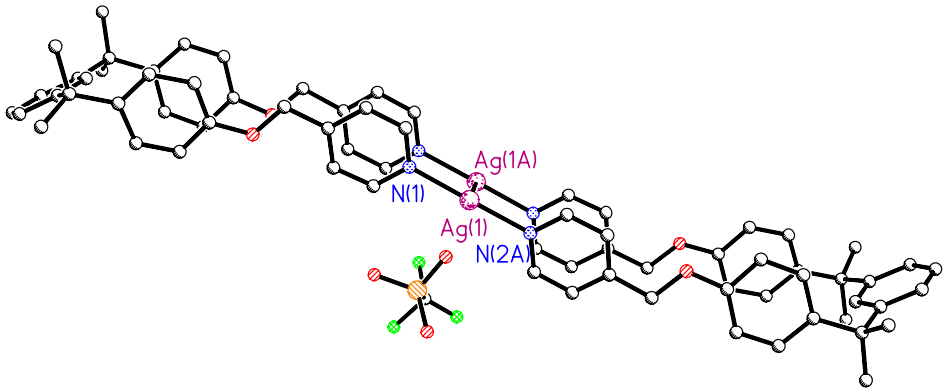


Figure 5.42 – *A side-on view of the silver dimetallic macrocycle* ***5.43****. Selected bond lengths (Å) and angles (°): Ag1-N1 2.140(7), Ag1-N2A 2.155(7), Ag1-Ag1A 3.199(2), N1-Ag1-N2A 172.4(3).*

Once again two U-shaped ligands and two silver atoms lie about a centre on inversion to give a large 52-membered rectangular dimetallic macrocycle, which is isomorphous to the other two silver macrocycles **5.41** and **5.42**, previously discussed. The nitrogen donor atoms, which are positioned at the tip of each U, coordinate to the silver atoms with a linear geometry and the Ag-N bond lengths are comparable. The U-shaped ligand components in **5.43** are similar to the other two silver macrocycles with the central benzene ring of the ligand positioned at the bottom of the U-shape with each of the spacer groups tilted in opposite directions, one up and one down. The distance across the length of the rectangle between spacer groups is 27.726Å and the intermetallic distance between the silver(I) atoms is 3.199Å. Both of these values are larger than those seen in the other two complexes (**5.41** and **5.42**) and the silver-silver bond is a little weaker. There are also π-π stacking interactions between the pyridine rings within a macrocycle (3.632Å), which are aligned almost parallel to one another.

A fourth silver rectangular dimetallic macrocycle was obtained with silver tetrafluoroborate, which crystallised in the space group P-1 with twice as much in the asymmetric unit in comparison to the other three complexes. The silver tetrafluoroborate complex had a similar overall topology to the three rectangular di-metallic macrocycles described above. The crystals of the silver tetrafluoroborate complex analysed as a 1:1 compound, which is the same stoichiometry as the other silver macrocycles.

*Crystal structure of the complex with $ZnBr_2$ (**5.44**)*

Slow evaporation of a methanol solution containing ligand **5.38** and zinc bromide produced colourless crystals suitable for X-ray crystallography. The structure solved in the orthorhombic space group Pbca revealing a one-dimensional helical coordination polymer. The asymmetric unit contains a whole ligand molecule and one $ZnBr_2$ unit. A section of the polymer showing its extended connectivity is shown in figure 5.43, with the hydrogen atoms excluded. The zinc atoms are 4-coordinate, being coordinated to the nitrogen atoms of two separate ligands and two bromide counterions with a distorted tetrahedral coordination geometry. The largest deviation from regular tetrahedral arises between the bromine atoms with an angle of 117.56° and the Zn-N bond lengths are similar to other reported complexes in this thesis.

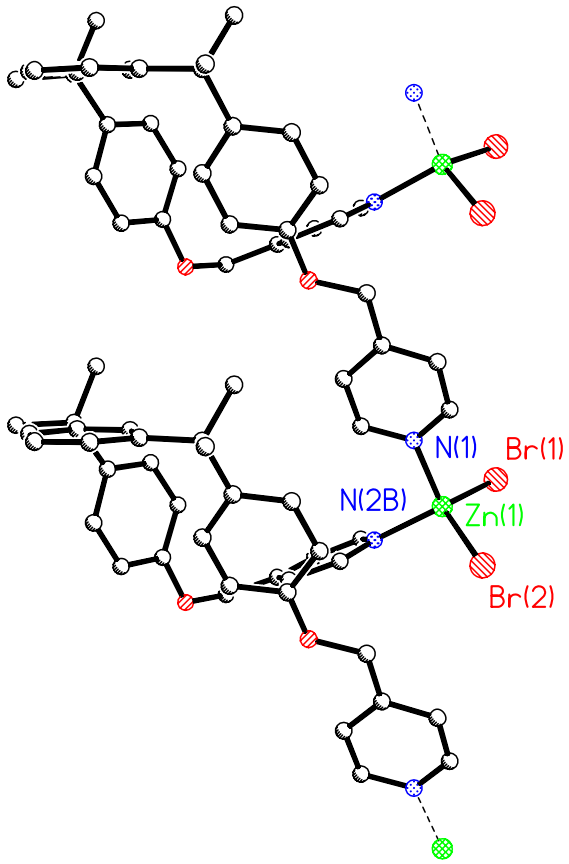


Figure 5.43 – *A section of the helical one-dimensional zinc coordination polymer **5.44**. Selected bond lengths (Å) and angles (°): Zn1-N1 2.054(1), Zn1-N2B 2.011(1), Zn1-Br1 2.350(2), Zn1-Br2 2.366(2), N2B-Zn1-N1 102.2(5), N1-Zn1-Br1 111.0(3), N2B-Zn1-Br1 111.7(4), N1-Zn1-Br2 104.4(3), N2B-Zn1-Br2 108.6(3), Br1-Zn1-Br2 117.56(9).*

The conformation of the ligand in complex **5.44** is a little different to the U-shaped conformation that ligand **5.38** adopted with the various silver salts, in which both of the binding arms of the ligand extended out in an *anti*-periplanar arrangement about the methyleneoxy group. In the zinc complex **5.44** the ligand adopts a similar U-shaped conformation with the bottom part of the U-shape formed by the central phenylene spacer unit. One of the arms of the U shape is extended out in an *anti* conformation with the pyridine ring and attached benzene ring almost coplanar to each other with an *anti*-periplanar arrangement about the methyleneoxy group with a C-C-O-C torsional angle of 175.8°. The other binding arm of the ligand adopts a g*auche* conformation in which the pyridine ring folds inwards. The ligand seems to adopt these conformations in the binding arms in order to twist around and coordinate to the zinc atoms in a helical manner.

The helical chains propagate along the a-axis of the unit cell with each section of the helix a translation from the previous. The complex crystallises in the centric space group Pbca and therefore contains both the left- (M) and right-handed (P) helices that are related by symmetry. A perspective view of the M-helix is depicted in figure 5.44, which emphasizes how the helicity of the helix is induced by the conformation of the ligand. The helices have a pitch of 8.489Å, which is the distance between two zinc atoms in a chain and equal to the length of the a-axis.

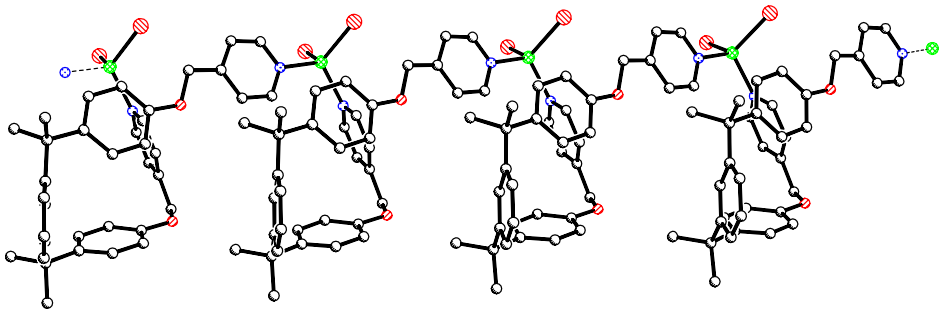


Figure 5.44 – *View of the M-helix in complex* ***5.44****.*

Within the helical chains there are edge-to-face interactions between the two pyridine rings that lie either side of the same zinc atom (2.640Å). There are also hydrogen bonding interactions between ligand molecules and bromine atoms that lie in the ranges of 2.806-3.028Å, involving both aromatic and methylene hydrogen atoms of the ligand.

*Other complexes with ligand **5.38***

The Bisphenol M derived ligand **5.38** was reacted with a variety of metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $Pd(PhCN)_2Cl_2$, $ZnCl_2$ and $ZnBr_2$ under a variety of conditions. Complexation of ligand **5.38** with various silver d^{10}-metal ions produced a series of four 52-membered silver dimetallic macrocycles, three of which were fully characterised by X-ray crystallography. Furthermore, by changing the metal ion to zinc that prefers a tetrahedral geometry, one obtains a completely different helical coordination polymer complex (**5.44**), as discussed above. This shows how the metal atom chosen can have a big influence over the assembly obtained. Unfortunately, crystals were not grown with all the metal salts and most of the complexes were precipitates or crystalline solids that were unable to be recrystallised.

Yellow precipitates formed immediately upon complexation of ligand **5.38** with the d^8-metals $PdCl_2$ and $Pd(PhCN)_2Cl_2$ that analysed as 1:1 compounds. This stoichiometry suggests the formation of a discrete complex which is perhaps similar in structure to the silver macrocycles. Palladium chloride complexes have a strong preference for square planar geometries and often form complexes with linear bridges between ligands and *trans*-coordinated chloride anions.

Reaction of ligand **5.38** with $Cu(ClO_4)_2$ gave a purple crystalline solid that analysed as a ML_2 compound. This could be a polymeric complex similar to the double necklace chain polymers previously reported with the metal salt $Cu(ClO_4)_2$ (**5.31**).

Complexes with ligand 5.39

*Crystal structure of the complex with $Cu(NO_3)_2$ (**5.45**)*

Ligand **5.39** and copper nitrate were both dissolved in methanol and combined. Slow evaporation of the resulting blue solution produced blue crystals that were suitable for X-ray crystallography. The complex crystallises in the monoclinic space group $P2_1/n$ with one ligand molecule, a half copper atom, one nitrate anion and a methanol molecule in the asymmetric unit. A perspective view of the asymmetric unit is shown in figure 5.45 with the hydrogens excluded for clarity. X-ray analysis of complex **5.45**

revealed a double chained necklace type polymer in which the ligand has an unusual weaving-like conformation about the metal centers.

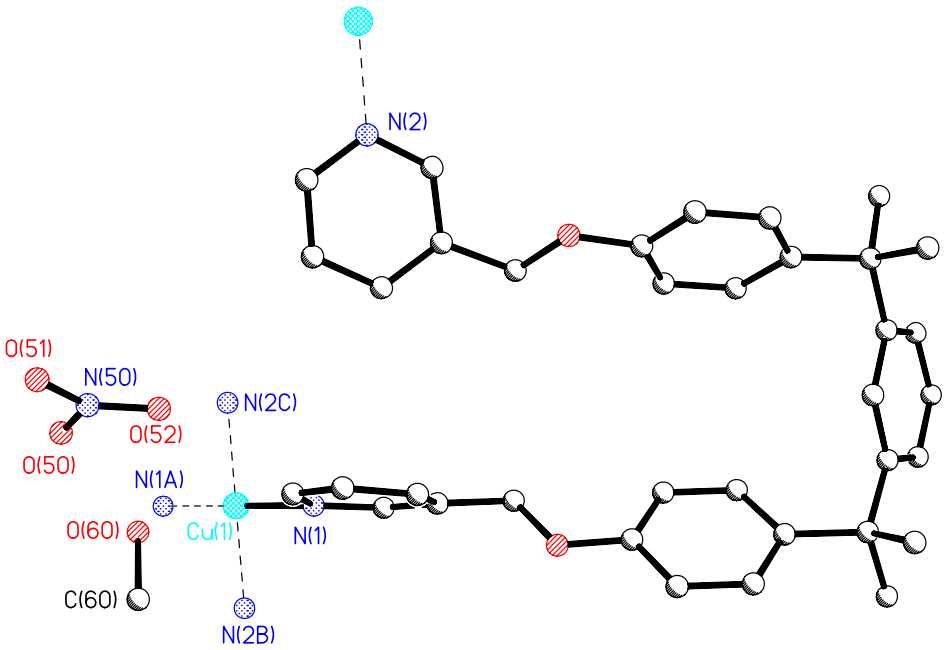


Figure 5.45 – *View of the contents in the asymmetric unit of complex* ***5.45****. Selected bond lengths (Å) and angles (°): Cu1-N1 2.068(3), Cu1-N2 2.016(3), N50-O50 1.270(4), N50-O51 1.216(4), N50-O52 1.233(4), O60-C60 1.565(9), N2B-Cu1-N1 92.5(1), N2B-Cu1-N1A 87.5(1), N1-Cu1-N1A 180.0(7), NB2-Cu1-N2C 180.0(1), N2C-Cu1-N1 87.5(1), N2C-Cu1-N1A 92.5(1), O51-N50-O52 122.9(4), O51-N50-O50 115.4(3), O52-N50-O50 121.5(3).*

In complex **5.45** the ligand adopts a similar U-shaped conformation to many of the other meta-substituted Bisphenol M derived ligands, with the phenylene ring positioned as the bottom part of the U-shape, as depicted in figure 5.45. Both of the arms of the ligand extend out in an *anti* conformation with the two pyridine rings tilted slightly perpendicular to the adjacent benzene rings with the nitrogen donor atoms pointing outwards. Intriguingly, the two terminal pyridine rings of the ligand are almost perpendicular with respect to one other, inclined at an angle of 72.48°, as seen in figure 5.45. Consequently, the two nitrogen donor atoms of the ligand are also perpendicular with respect to each other.

In the structure the copper(II) atoms lie on a crystallographic centre of inversion. Each of the copper(II) atoms is coordinated to four nitrogen atoms from separate U-shaped

ligands and through the oxygen atom of two methanol molecules with an overall pseudo-octahedral coordination geometry. The equatorial plane is occupied by the four pyridine nitrogens from different ligands with Cu-N bond distances of 2.068Å and 2.016Å. The axial positions are occupied by the oxygen atoms from two methanol molecules with a Cu-O bond length of 2.490Å. The two methanol molecules have significantly longer bond lengths to the equatorial ones, which therefore indicates the occurrence of Jahn-Teller distortion about the copper(II) centers. A search of the literature revealed only a few complexes with a similar copper(II) geometry coordinated to four nitrogen atoms and two methanol molecules.[305-308]

The resulting complex is a double chained necklace-type polymer that propagates along the ac-diagonal of the unit cell, in which the ligand has an unusual weaving-like conformation about the copper metal centers. The overall topology of this necklace-like polymer complex is depicted in figure 5.46. Two U-shaped ligands bond to two copper atoms to give a M_2L_2 macrocycle, with a distance between copper atoms across the macrocycle of 9.862Å. The weaving-like conformation is due to the orientations of the pyridine rings. The pyridine rings of the two coordinated ligands in a M_2L_2 macrocycle are in a *cis*-relationhip on the copper atom. As a consequence of the conformation of the ligand and overall topology of the complex there are no π-π stacking interactions between the aromatic rings within a macrocycle. The absence of such π-π stacking within a macrocycle is unusual, because such interactions are known to stablise the structure.

In the extended structure the one-dimensional necklace polymer chains stack down the a-axis of the unit cell, with a distance between copper atoms in a stack of 8.823Å, which is the length of the a-axis. Furthermore, the necklace polymer chains are not interpenetrated due to the conformation of the U-shaped bridging ligands and absence of an internal cavity. In general in order for polymers to interpenetrate and encapsulate various solvent molecules one needs a larger cavity. The oxygen atoms of the nitrate anions are involved in numerous C-H···O interactions with ligand hydrogen atoms and the coordinated methanol solvent molecules, with distances ranging between 2.245Å and 2.679Å.

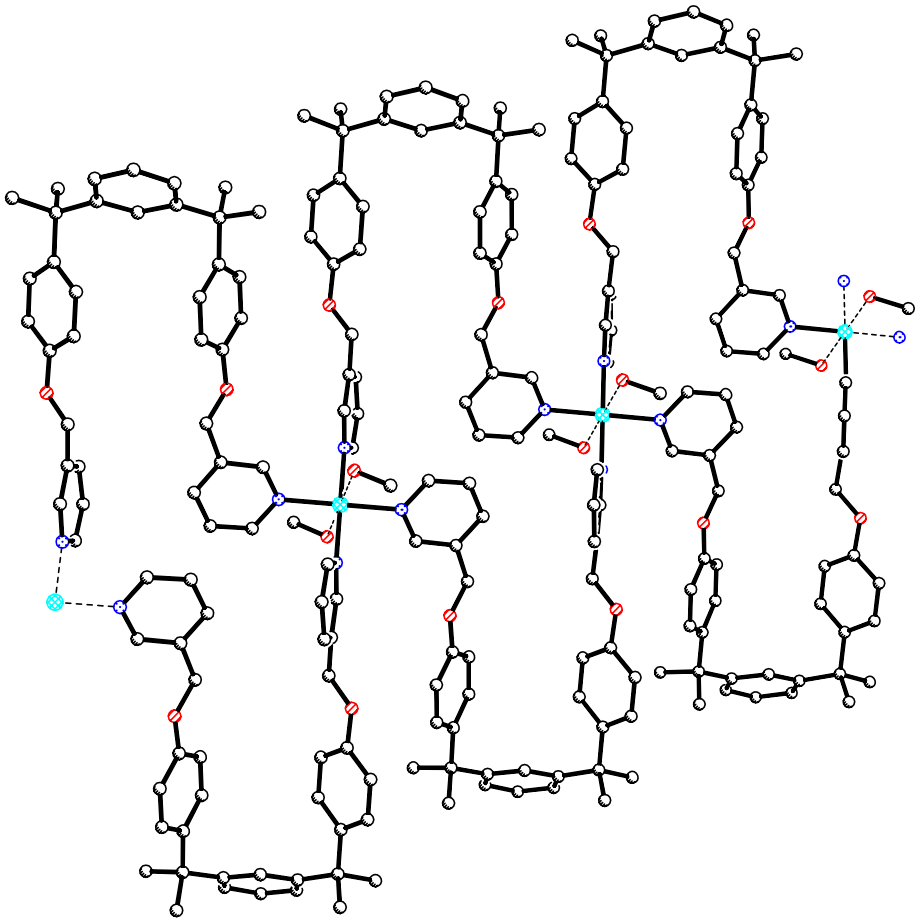


Figure 5.46 – *A section of the one-dimensional necklace polymer* ***5.45****.*

The necklace-like topology of complex **5.45** is very similar to the necklace topology generated with the pyrazine substituted Bisphenol M derived ligand **5.23** and copper perchlorate (**5.31**). The copper centers of both necklace polymers have pseudo-octahedral coordination geometries with Jahn-Teller distortion due to the longer axial bond lengths. The main difference between the two necklace polymers is the overall shape of the necklace. Complex **5.31** has more square-like M_2L_2 macrocyclic units, whereas complex **5.45** has rectangular-like M_2L_2 macrocyclic units as a consequence of the U-shaped ligands that weave along the necklace polymer chain.

*Crystal structure of the complex with $ZnBr_2$ (**5.46**)*

Slow evaporation of a solution containing zinc bromide and ligand **5.39** produced colourless crystals of a zinc bromide complex (**5.46**) suitable for X-ray crystallography.

The structure solved in the triclinic space-group P-1 and X-ray analysis revealed a one-dimensional zig-zag chain. The asymmetric unit contains two ligand molecules, two zinc bromide units and a dichloromethane solvent molecule, as shown in figure 5.47, with the hydrogens and solvent molecule excluded for clarity.

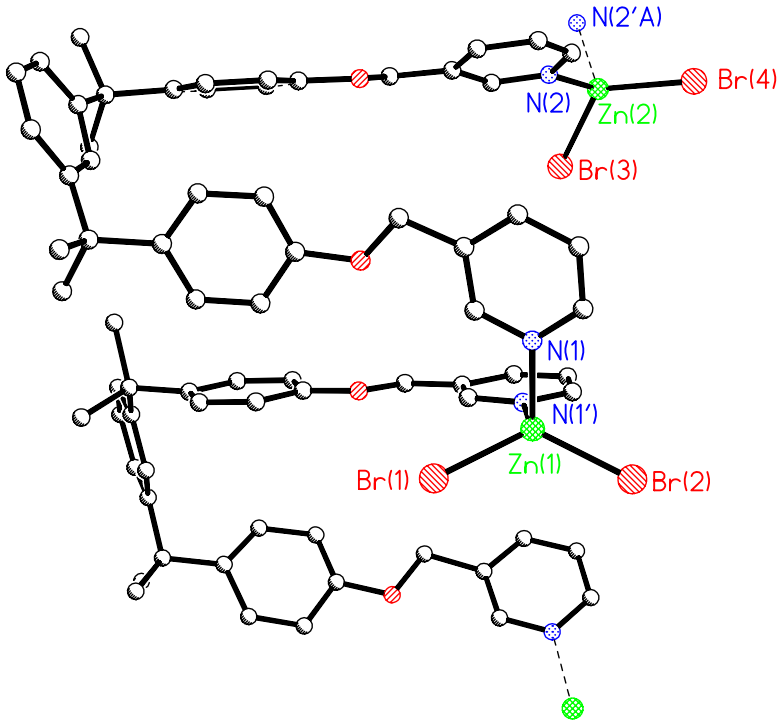
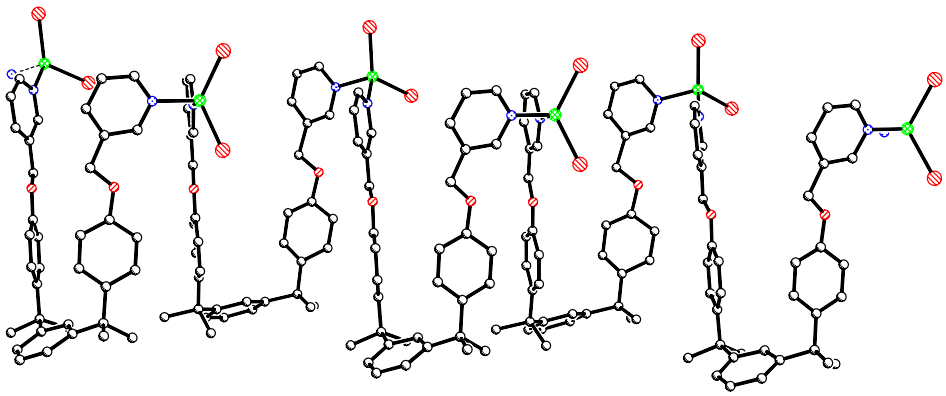


Figure 5.47 – *View of the contents of the asymmetric unit of complex* ***5.46****. Selected bond lengths (Å) and angles (°): Zn1-N1 2.044(5), Zn1-N1' 2.054(5), Zn1-Br1 2.375(1), Zn1-Br2 2.343(1), Zn2-N2 2.050(6), Zn2-N2'A 2.053(6), Zn2-Br3 2.345(1), Zn2-Br4 2.342(1), N1-Zn1-N1' 100.1(2), N1-Zn1-Br2 110.5(2), N1'-Zn1-Br2 109.2(2), N1-Zn1-Br1 105.9(2), N1'-Zn1-Br1 105.9(1), Br2-Zn1-Br1 122.87(4), N2-Zn2-N2'A 101.2(2), N2-Zn2-Br4 107.5(1), N2'A-Zn2-Br4 109.7(2), N2-Zn2-Br3 106.9(2), N2'A-Zn2-Br3 105.5(2), Br4-Zn2-Br3 123.70(5).*

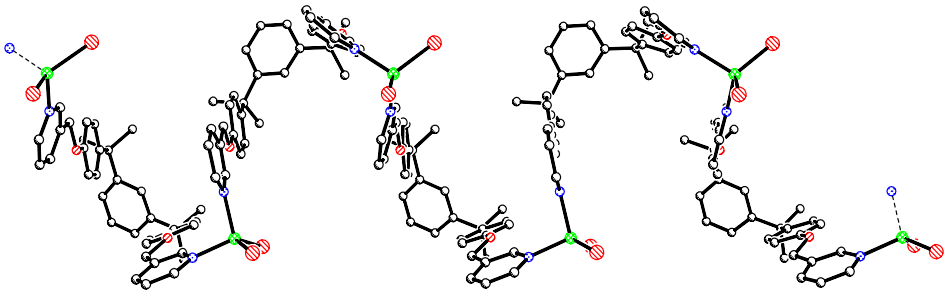
Each of the ligands adopts a U-shaped conformation in complex **5.46**, in which the bottom half of the U-shape is formed by the central phenylene ring. Both of the arms of the U-shaped ligands extend out with the pyridine rings almost coplanar with the attached benzene ring in an *anti* conformation. Also, both of the nitrogen donor atoms from each of the ligands point outwards in the same direction in order to bind to the zinc atoms. The two U-shaped ligands in the asymmetric unit are connected to one another through the zinc metal centres; both oriented in the same direction and rotated approximately 90° with respect to each other. The two U-shaped ligands are not

identical to each other and there are subtle differences between the two ligand conformations. Both of the zinc atoms have a distorted tetrahedral geometry with the largest deviation from tetrahedral at both metal centers occurring between the bromine atoms.

The resulting complex is a zig-zag chain that propagates in one dimension by translation. Two different views of a section of the zig-zag chain are depicted in figure 5.48, with the hydrogens and solvent molecules removed for clarity. The view illustrated in figure 5.48(a) is a side-on view of the complex along the b-axis and the view in figure 5.48(b) is a birds-eye view of the complex when looking down the c-axis of the unit cell through the zinc metal atoms. The second view of **5.46** shows the polymer to have an undulating, almost corrugated appearance.



(a)



(b)

Figure 5.48 – *Two different views of the undulating zig-zag structure of complex* ***5.46****.* ***(a)*** *Side-on view of complex* ***5.46*** *along the b-axis* ***(b)*** *Birds-eye view of* ***5.46****.*

In the extended structure the polymer strands pack closely together with numerous edge-to-face interactions between aromatic rings and C-H···π interactions between methylene hydrogens and aromatic rings. There are hydrogen bonding interactions between aromatic and methylene hydrogens of the ligand and bromine atoms of 2.926Å and 3.034Å. The bromine atoms also make short contacts with the hydrogen atoms of the dichloromethane solvent molecules of 2.647Å and 2.914Å. The dichloromethane solvent molecules also make other short contacts with the polymer strands.

*Crystal structure of the complex with $ZnCl_2$ (**5.47**)*

An almost identical zinc zig-zag polymer chain to **5.46** was prepared from ligand **5.39** and zinc chloride under exactly the same solvent conditions. However, these colourless crystals had completely different cell constants and solved in the monoclinic space group P2/n. The asymmetric unit of complex **5.47** contains two whole ligand molecules, two zinc atoms, four bromine atoms and two half dichloromethane solvent molecules that are on special positions. A view of the asymmetric unit from a different orientation to complex **5.46** is shown in figure 5.49 to illustrate how the two U-shaped ligands are rotated approximately 90° to one another within the asymmetric unit. Excluded for clarity are the hydrogen atoms and the dichloromethane solvent molecules. The two half dichloromethane solvent molecules are located on special positions that grow into whole dichloromethane molecules about a two-fold rotation axis. Unfortunately, the crystals were very thin plates of poor quality that gave poor diffraction patterns. As a consequence the structure refined poorly, giving a final R_1 value of 11.53%. However, since the zinc chloride complex is analogous to the previously discussed zinc bromide complex with exactly the same topology, no further analyses was done.

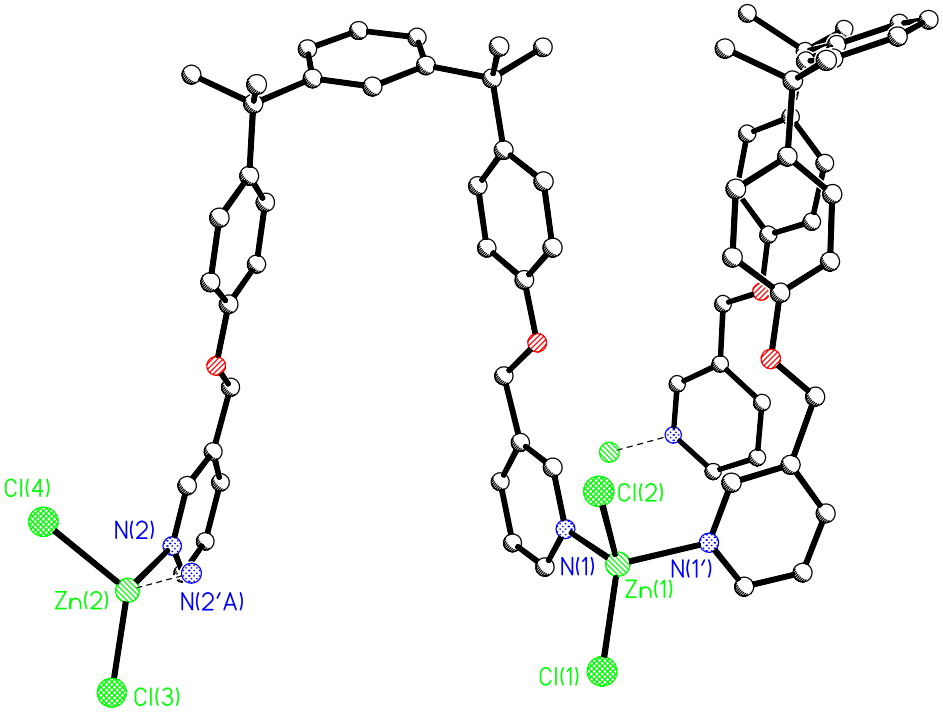


Figure 5.49 – *Perspective view of the contents of the asymmetric unit of complex* ***5.47****. Selected bond lengths (Å) and angles (°): Zn1-N1 2.054(9), Zn1-N1' 2.041(8), Zn1-Cl1 2.202(3), Zn1-Cl2 2.217(3), Zn2-N2 2.035(8), Zn2-N2'A 2.052(9), Zn2-Cl3 2.168(5), Zn2-Cl4 2.268(6), N1'-Zn1-N1 100.5(3), N1-Zn1-Cl1 110.0(3), N1'-Zn1-Cl1 112.2(2), N1-Zn1-Cl2 104.1(3), N1'-Zn1-Cl2 104.0(2), Cl1-Zn1-Cl2 123.42(13), N2-Zn2-N2'A 102.9(3), N2-Zn2-Cl3 112.8(3), N2'A-Zn2-Cl3 112.0(3), N2-Zn2-Cl4 102.1(3), N2'A-Zn2-Cl4 102.4(3), Cl3-Zn2-Cl4 122.4(3).*

Both complexes have the same contents in the asymmetric unit with a similar zig-zag topology with different counterions being the only difference between the two polymers. Both of the zinc atoms in the asymmetric unit of complex **5.47** are 4-coordinate, being coordinated by the pyridine nitrogen atoms of two separate ligands and two chlorine atoms. The coordination geometry of each of the zinc atoms is distorted tetrahedral with the largest distortion arising between the chlorine atoms. Both ligands adopt the same U-shaped conformation as the zinc bromide complex (**5.46**) with the central phenylene group positioned at the bottom of the U-shape. As a consequence of this conformation the binding arms of the ligand extend out in an *anti* conformation with the pyridine rings and attached benzene rings almost coplanar with one another. Once again, both of the U-shaped ligands within the asymmetric unit are rotated approximately 90° to each other on either side of the Zn1 atom, as illustrated in figure

5.49. As expected the Zn-N bond lengths are very similar to bond lengths observed in the zinc bromide complex **5.46**, and the Zn-Cl bond lengths are also within the same range of other zinc chloride complexes in this thesis. The zig-zag polymer **5.47** propagates along the a-axis by translation, in a similar fashion to the zinc bromide complex **5.46**.

*Other complexes with ligand **5.39***

Ligand **5.39** was reacted with a variety of metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $Pd(PhCN)_2Cl_2$, $ZnCl_2$ and $ZnBr_2$. Three of these metal salts upon complexation produced crystals suitable for X-ray analysis. Two zig-zag polymers formed with the zinc metals $ZnCl_2$ and $ZnBr_2$, and a unique copper(II) double necklace chain formed with $Cu(ClO_4)_2$. Unfortunately, crystals were not grown with all the metal salts and most of the complexes gave precipitates immediately that were unable to be recrystallised. A few of these precipitates were analysed by elemental analysis.

A green precipitate formed immediately upon complexation of ligand **5.39** with $CuCl_2$ that analysed as a M_3L_2 compound with no solvent.

Reaction of $PdCl_2$ with ligand **5.39** gave a yellow precipitate immediately. Elemental analysis revealed a 1:1 ratio. Reaction of ligand **5.39** with $Pd(PhCN)_2Cl_2$ analysed as a Pd_2L_2 compound.

Complexes with ligand 5.40

Ligand **5.40** was reacted with a variety of metal salts, such as $CoBr_2$, $CoCl_2$, $CuCl_2$, CuI, $Cu(NO_3)_2$, $Cu(ClO_4)_2$, $CuSO_4$, $AgPF_6$, $AgBF_4$, $AgClO_4$, $AgCF_3SO_3$, $PdCl_2$, $Pd(PhCN)_2Cl_2$, $ZnCl_2$ and $ZnBr_2$. Regrettably, no crystals suitable for X-ray crystallography were obtained and mainly insoluble precipitates were formed. Attempts were made to recrystallise the precipitates; however despite numerous attempts no crystalline solids or crystals were obtained.

Slow evaporation of a solution containing ligand **5.40** and $CuCl_2$ generated a pale green solid that analysed as a M_2L compound. A yellow precipitate formed immediately upon complexation of ligand **5.40** with the d^8-metal $PdCl_2$ that analysed with a 1:1 stoichiometry. Reaction of ligand **5.40** with $Pd(PhCN)_2Cl_2$ gave a yellow crystalline solid after evaporation of the solution to dryness. The crystalline solid analysed as a M_3L_2 compound.

Summary

This chapter described two new series of ligands based around the Bisphenol P and Bisphenol M cores. The new bridging ligands were even more flexible than the Bisphenol A and Bisphenol Z derived ligands due to the incorporation of an additional spacer unit into the ligand structure. It was anticipated that the incorporation of an extra phenylene spacer group into the ligand structure could lead to a larger number of different and fascinating supramolecular assemblies. In this chapter, fourteen new ligands were synthesised and the X-ray structures of eight of these were determined. The Bisphenol P and Bisphenol M derived ligands were subsequently reacted with various metal salts to give a wide variety of both discrete and polymeric complexes that were able to be crystallised and fully characterised by X-ray crystallography.

The Bisphenol P based ligands proved to be useful synthons for the construction of metallosupramolecular species. Ligand **5.10** formed two zig-zag polymers with $CoBr_2$ and $CoCl_2$ that had similar topologies. The pyrazine substituted Bisphenol P ligand **5.11** formed an intriguing complex composed of three ligand strands that are linked by Cu_3Cl_6 bridging motifs into a two-dimensional sheet that had large cavities of approximately 18Å in diameter. Numerous complexes formed with the methyleneoxy extended ligands **5.17**, **5.18** and **5.19**, although many did not crystallise due to insolubility. Consequently, only one complex was fully characterised by X-ray crystallography, viz **5.18**, a one-dimensional coordination polymer. Unfortunately, no complexes with ligands **5.12** and **5.13**, containing the larger heterocyclic rings quinoline and quinoxaline, were able to be crystallised.

The Bisphenol M based bridging ligands proved to be even more versatile ligands than the Bisphenol P derived bridging ligands, generating diverse discrete and polymeric

complexes. Ligand **5.22** formed a unique double-chained necklace polymer with copper perchlorate and then a unique silver chain of chelate rings in which the ligand coordinates through internal nitrogen atoms whilst the external nitrogens bridge into an external chain. A similar silver chain of chelate rings was also generated with silver perchlorate.

The quinoline substituted Bisphenol M ligand **5.24** generated a selection of large discrete 20-membered chelate rings. In each of the complexes the ligand adopted the same U-shaped conformation with the quinoline rings perpendicular to the attached benzene rings with the nitrogen atoms facing inwards to chelate to the silver atom. The quinoline rings are almost coplanar to each other in all the chelate rings with the mean planes all tilted by less than 20°. In all the complexes the ligand chelates to the metal atom in a trans-spanning arrangement, as a consequence of the flexibility of the meta-substitution about the central benzene ring. One of the discrete complexes also included the decomposition of a hexafluorophosphate anion to a $PO_2F_2^-$ anion. Unfortunately, no complexes with ligand **5.25** were crystallised.

Extension of the Bisphenol M derived ligands with methyleneoxy two-atom spacer groups was also investigated. The flexibility of this group of ligands led to a range of products both discrete and polymeric, some of which were able to be fully characterised by X-ray crystallography. The most interesting structures are a series of 52-membered silver dimetallic macrocycles with ligand **5.38** and various silver d^{10}-metal salts that exhibit weak inter-metallic bonds between the two silver atoms. What is intriguing is that, if one changes the metal ion to a smaller zinc cation that prefers a tetrahedral geometry, one obtains a one-dimensional helical coordination polymer. This clearly illustrates the inherent flexibility of ligand **5.38** with its ability to adopt different conformations depending on the metal atom chosen and emphasises how the products obtained cannot be predicted. Ligand **5.39** formed zig-zag polymers with the zinc metals $ZnCl_2$ and $ZnBr_2$, and a copper necklace-like chain with $Cu(ClO_4)_2$.

Many different conformations were observed with the ligands in the solid state and in their complexes. There does not seem to be a preference for any particular preorganised conformation of the ligand in the complexes, which is inherently due to the extra flexibility of these ligands.

Chapter Six

Conclusion

Conclusion

This thesis described the synthesis and coordination chemistry of forty-eight bridging ligands, one of which had previously been reported. All of the forty-eight ligands reported in this work contained nitrogen heterocyclic groups. The majority of the ligands synthesised were based around commercially available bisphenol cores and were designed to act as synthons in metallosupramolecular chemistry by reactions with a variety of transition metal atoms. By varying the nature of the organic ligand and the transition metal precursor used, a range of supramolecular topologies and architectures were formed. To date a great deal of study has focused on rigid ligands as the components for the construction of metallosupramolecular assemblies. In contrast, less emphasis has been placed on ligands of a flexible nature and therefore this research focused on such ligands. Ligands can be made more flexible by the introduction of flexible spacer groups between the ligand core and the donor heterocyclic group, which are usually constructed from combinations of methylene groups with oxygen or sulfur atoms. A lot of study has focused on the use of rigid ligands as building blocks in metallosupramolecular assemblies, due to the control and predictability the chemist has over the products formed. As a result the complexes formed tend to be more symmetrical, such as polygons. In contrast, ligands that are flexible in nature take away some of the control and predictability of the products by adding more variables into the system. The result is therefore often a product that was not initially predicted. Flexible ligands often form less symmetrical, but more exciting topologies, such as cages, rectangles and helicates in comparison to their rigid ligand counterparts. Therefore, this research focused on flexible ligands, due to their unpredictability and potentially interesting less symmetrical complexes.

For many years the Steel group has been synthesising ligands and their various complexes based around heterocyclic rings linked to an aromatic group via flexible spacer groups. Previous members of the Steel group have modified all or some parts of a basic generalised core in order to synthesise a large range of flexible ligands. A majority of the flexible ligands have been based around a single rigid benzene ring as the central core unit, which is linked to nitrogen containing heterocyclic groups via various flexible spacer groups, such as oxygen atoms and methylene groups. Although,

the majority of ligands contain benzene as the central core, other larger aromatic ring systems have been employed, such as naphthalene, biphenyls and anthracene. In contrast, there has been very little research done on symmetrical flexible ligands based around two or more independent benzene rings attached via flexible spacer groups to separate nitrogen heterocycles. Therefore, this research set out to synthesise and explore such flexible ligands and their coordination chemistry. Two simple ligand cores that exemplify this are Bisphenol A and Bisphenol Z, which just like the other bisphenols, have been rather neglected in the literature as ligand backbones. As a consequence, ligands based around such bisphenol based cores seemed ideal for a new range of flexible symmetrical ligands.

To begin this research a range of flexible two-armed bridging ligands were synthesised based around Bisphenol A, Bisphenol Z and Bisphenol AP ligand cores, with the Bisphenol AP ligands being less symmetrical than the other two. Next a range of larger flexible two-armed ligands based around the Bisphenol P and Bisphenol M cores were synthesised that were even more flexible than the previously mentioned bisphenol bridging ligands, due to the incorporation of an additional spacer group within the structure. Finally, a range of multi-armed ligands were synthesised. To keep with the theme of using phenols within the ligands structure, a series of three-armed ligands based around a central trisphenol core were produced. All of the ligands synthesised contained nitrogen heterocyclic groups appended to the central core unit via one- or two-atom flexible spacer groups.

The Bisphenol A based ligands were designed around a Bisphenol A backbone, which consisted of a central rigid propane group coordinated to two separate benzene rings. Crystal structures of many of these ligands were obtained, confirming their structures and overall conformations in the solid state. As anticipated all of the ligands had a ‘V-type’ arrangement, with the two aromatic benzene rings acting as the arms of the ‘V’.

The Bisphenol A based ligands proved very successful as synthons in metallosupramolecular chemistry by the formation of a number of interesting and diverse coordination complexes. Indeed, one of the most versatile ligands was the 2-substituted pyridine ligand **2.19**, which formed a variety of complexes many of which were fully characterised by X-ray crystallography. There was a large range of quite different complexes formed with ligand **2.19**, which demonstrates the unpredictable

nature of these systems. It formed a one-dimensional coordination polymer with $CoBr_2$, an interesting necklace-like double chain with $CuCl_2$, several one-dimensional helical polymers and several [2+2] macrocycles with various metal salts. However, by far the most fascinating complex was the formation of the copper(II) dinuclear quadruple helicate made from $Cu(NO_3)_2$. To the best of our knowledge this is the first example of a dinuclear quadruply-stranded helicate with square-pyramidal termini. Initial investigations into the quadruple helicate determined that there was a small void inside the central cavity, although there was no indication of any guest molecule(s) inside the cavity. However, it would be interesting in future studies to examine the host-guest chemistry of this compound.

Compared to ligand **2.19**, the other Bisphenol A based ligands were not as versatile, but were still relatively good synthons for metallosupramolecular chemistry. The rest of the Bisphenol A based ligands formed insoluble complexes, which did not seem to crystallise as readily as the complexes with ligand **2.19**. As a consequence, only three other complexes were fully characterised. X-ray analysis revealed the formation of two one-dimensional polymeric structures and a discrete [2+2] macrocycle with the pyrazine substituted ligand **2.21**. Unfortunately, no crystals of any complexes were obtained with the ligands **2.23** and **2.25** containing the larger heterocyclic ring systems quinoline and quinoxaline. This could be due to the increased steric bulk around the Bisphenol A core causing low solubility in these ligands. It would be interesting to investigate these ligands and their corresponding complexes again in the future by employing other techniques to grow crystals like H-tubes and U-tubes.

A series of two-armed bridging ligands were synthesised based around a Bisphenol Z core, which also proved to be versatile synthons for the construction of metallosupramolecular assemblies. Once again crystal structures of many of the ligands themselves were obtained and as anticipated the shape of the ligands was very similar to that of the Bisphenol A ligands with a ‘V-type’ arrangement, with the two benzene groups acting as the arms of the V.

Many of the complexes obtained formed with the 2-substituted pyridine ligand **2.53**. The majority of the complexes isolated with ligand **2.53** had one-dimensional helical polymeric structures. Interestingly, it was found that the two zinc helical coordination polymers were found to be isomorphous to each other. Also, a double-chain necklace

polymer formed with $CuCl_2$ and ligand **2.53** that displayed a copper motif with copper atoms in two different coordination environments. Two double-chain necklace-like polymers also formed with the pyrazine substituted ligand **2.54**, which had distinctly different topologies.

Complexes with ligands **2.55** and **2.56** containing the bulkier π ring systems, quinoline and quinoxaline, appended to the Bisphenol Z based core were unable to be crystallised. Once again this appears to be due to the low solubility of the ligands and complexes. Hopefully such problems might be overcome in the future by adopting other crystallisation techniques.

Three more Bisphenol Z based ligands were synthesised that were even more flexible containing two-atom methyleneoxy spacer groups. These ligands proved to be versatile synthons for metallosupramolecular chemistry by the formation of both discrete and polymeric structures. The 3-substituted pyridine ligand **2.68** formed a discrete [2+2] macrocycle with $ZnCl_2$, whereas the 2-substituted pyridine ligand **2.69** seemed to prefer to form polymeric coordination structures. All of the coordination polymers formed with ligand **2.69** were different from one another, demonstrating the versatility of the ligand as a synthon in metallosupramolecular chemistry. Interestingly, all the complexes formed with the two-atom spacer group exhibited both *anti* and *gauche* conformations in the binding arms of the ligand. All in all the Bisphenol Z based ligands were successful synthons for the construction of a diverse range of complexes. Future studies with these ligands could include investigations into the coordination chemistry with other metals, such as the rare earth elements like lanthanum(III).

Chapter three described the synthesis and coordination chemistry of a series of less symmetrical two-armed bridging ligands based around a Bisphenol AP core. The Bisphenol AP ligands contained a single quaternary carbon atom as the central core with three benzene rings and a methyl substituent group tethered from it. Only two of the benzene rings were further linked to nitrogen containing heterocyclic groups via one- or two-atom spacer groups, leaving the third benzene ring pendent. Previous studies have shown that complexes with less symmetrical ligands are harder to crystallise as a result of the less symmetrical structure of the ligands, often giving a mixture of products. Therefore, it was probable that any complexes made with the Bisphenol AP ligands would be difficult to crystallise. Indeed, this was the case and

only one complex was crystallised and fully characterised by X-ray crystallography. It was also anticipated that the pendent benzene ring could participate in cation-π interactions with various metal ions, thus potentially further stabilising any complexes formed. Unfortunately, this was not seen in the complex and hopefully in the future studies will investigate this further.

The final chapter in this thesis describes the synthesis and coordination chemistry of another two series of two-armed bridging ligands derived around the larger Bisphenol P and Bisphenol M cores. These ligands were larger and even more flexible than the Bisphenol A and Bisphenol Z derived ligands, due to the incorporation of additional spacer units into the ligand structure. Once again crystal structures of many ligands were obtained, which often gave a good indication of the flexibility of the ligand and therefore its ability to form complexes. The difference between the Bisphenol P and Bisphenol M cores is the substitution of the ligand arms around the central spacer unit. The Bisphenol P derived bridging ligands have a 1,4-substitution around the central phenylene ring, whereas the Bisphenol M derived ligands have a 1,3-substitution pattern.

It was initially assumed that this very slight difference in substitution around the central phenylene ring would have little or no effect on the preparation and crystallisation of various complexes. However, as it turned out the differing substitution patterns around the central phenylene ring did have an effect on the crystallisation of complexes with the complexes with Bisphenol M crystallising more readily than the Bisphenol P complexes.

In general, the majority of the complexes obtained with the Bisphenol P based ligands in this study had one-dimensional polymeric structures. However, the pyrazine substituted ligand **5.11** did form an elaborate complex with $CuCl_2$, which was composed of three ligand strands that were linked by Cu_3Cl_6 bridging motifs into a two-dimensional sheet. Numerous attempts were undertaken to crystallise other complexes with these ligands with no success and perhaps future research workers may have more success in growing crystals with these ligands using different techniques.

On the other hand, the Bisphenol M derived bridging ligands proved to be very useful in this research by forming a large assortment of complexes, many of which crystallised

easily. The characterisation of both discrete and polymeric structures demonstrates the unpredictable nature of the products with these ligands. A good example of the unpredictability of these systems is illustrated with the pyrazine substituted ligand **5.22**, which formed a double-chained complex with $Cu(ClO_4)_2$ and then a chain of chelate rings with $AgPF_6$, in which the ligand coordinates through the internal nitrogens, while the external nitrogens bridge to form a polymeric chain.

A series of discrete 20-memebered chelate rings was synthesised with the quinoline substituted Bisphenol M derived ligand **5.24** with copper and silver salts. In all the complexes the ligand chelates to the metal atom in a trans-spanning arrangement. Interestingly, one of the complexes included the decomposition of a hexafluorophosphate anion to a rare $PO_2F_2^-$ anion.

The Bisphenol M ligands with the incorporation of a two-atom spacer group were also found to be just as versatile to this research by forming many different complexes. The added flexibility in the ligands led to a range of both discrete and polymeric structures. A series of unique 52-membered silver dimetallic macrocycles was fully characterised with the 4-substituted ligand **5.38** and various silver salts that exhibited weak inter-metallic bonds between the two silver atoms. Subsequently, a one-dimensional helical coordination polymer was obtained with the same ligand **5.38** and $ZnBr_2$, which clearly demonstrates the unpredictability of the products with such flexible ligands. The rest of the complexes crystallised with the Bisphenol M based ligands in this study had one-dimensional polymeric structures.

Multi-armed ligands are very topical in metallosupramolecular chemistry, because they have multiple coordination sites that are capable of binding and bridging multiple metal atoms often resulting in more spectacular assemblies. Therefore, attempts were made to design and synthesise series of three-armed, four-armed and six-armed ligands based around different cores with a variety of heterocyclic groups attached via one- or two-atom spacer groups.

A series of seven three-armed ligands based around a trisphenol core were synthesised with various heterocyclic groups attached to the central core unit via one- or two-atom spacer groups. The trisphenol ligands were quite large ligands, each containing six aromatic rings. The coordination chemistry of these tripodal ligands was investigated

and two crystal structures of complexes were obtained, one discrete and one polymeric. The polymeric complex was generated with the pyrazine substituted ligand **4.16** and CuI, in which only two of the three ligand arms coordinates to metal centers. Reaction of the pyridine substituted ligand **4.15** with $CuCl_2$ produced a discrete M_3L_2 cage complex that was another high point to this research. This result was exciting because one of the reasons for synthesising three-armed ligands was to construct complicated cage-like species. The M_3L_2 cage appears to be quite flat, as a result of the splayed out conformation of the ligand and as a consequence there is no central cavity. This flattening in the complex could be a result of the flexibility in the ligand. It is possible that reaction of this same ligand with other appropriate metal salts could lead to the self-assembly of similar cages with a cavity inside that could allow the encapsulation of a guest molecule. However, no other M_3L_2 cages were made with ligand **4.15** during the rest of this research and therefore no further investigations were done, but hopefully this will be re-examined in the future. No other complexes were fully characterised with the other three-armed ligands, due to the low solubility of the ligands and their complexes in most solvents.

A family of four-armed ligands was synthesised, based on a 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol core. Unfortunately, despite numerous attempts, no complexes containing these ligands could be characterised for X-ray analysis. Hopefully, in the future crystals of complexes with these ligands can be obtained as these ligands are likely to act as exciting synthons in metallosupramolecular chemistry. Attempts were also made to synthesise two other ligand families based around the tetrakis(4-hydroxyphenyl)methane and 1,1,4,4-tetrakis(4-hydroxyphenyl)cyclohexane cores. Unfortunately, the syntheses of the required ligand precursors were unsuccessful and therefore no further reactions were carried out. Once again this was disappointing, because ligands based around these cores could potentially be exciting synthons in metallosupramolecular chemistry. Hopefully this will also be re-examined in the future.

The last section of chapter four discussed a family of six-armed ligands based around a dipentaerythritol core. The Steel group has synthesised and investigated the coordination chemistry of several hexa-substituted ligands over the years, most of which are based around an aromatic core. Unfortunately, the last step involving the substitution of the various heterocyclic groups onto the dipentaerythritol core was

unsuccessful and as a consequence the coordination chemistry of none of these ligands was studied further. Once again this was rather disappointing and hopefully in the future further attempts will be made.

X-ray crystallography is the best technique available to fully characterise a compound and therefore it has been used extensively in this research to characterise the complexes. However, other techniques could also be used in the future to study the properties of these characterised complexes, such as spectroscopy, NMR and thermogravimetric analysis (TGA).

The X-ray analysis of so many compounds allows one to also investigate hydrogen bonding interactions and other secondary interactions between the components of the assemblies. Hydrogen bonding interactions occurred extensively in many of the compounds in this thesis, often between solvent molecules and coordinated molecules in complexes. There were also numerous examples of π-π stacking interactions between ligand molecules throughout this thesis. Examples of both face-to-face and edge-to-face interactions were observed with there being more examples of edge-to-face interactions.

This thesis described the synthesis of forty-eight new ligands all based around nitrogen containing heterocyclic rings. The X-ray crystal structures of twenty-seven of these ligands were obtained and discussed. The new ligands were reacted with a variety of metal salts in the hope of generating novel metallosupramolecular assemblies. This was successful and numerous complexes formed. Subsequently, crystals suitable for X-ray crystallography were obtained for forty-three of these complexes. Undoubtedly this research could have been improved further if more complexes had been crystallised and fully characterised by X-ray crystallography. A diverse range of complexes with these ligands were fully characterised, exemplifying the unpredictability and wonder of metallosupramolecular chemistry. It is anticipated that the coordination chemistry presented in this thesis is just the beginning of the work that can be done with these ligands and, hopefully, other workers in the future will employ these ligands as supramolecular synthons.

Chapter Seven

Experimental

Chapter Seven

Experimental

General experimental

^{1}H NMR spectra were recorded on Varian Unity 300 or Varian 500 spectrometers at 23°C with a 3mm probe operating at 300MHz or 500MHz. ^{1}H NMR spectra recorded in $CDCl_3$ were referenced relative to the internal standard Me_4Si and those recorded in deuterated dimethyl sulfoxide were referenced against the solvent signals at 2.6 ppm. ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer at 23°C with a 3mm probe operating at 75MHz. ^{13}C NMR spectra recorded in $CDCl_3$ were referenced against the solvent signal at 77.10ppm. When required ^{1}H nOe, 1-D TOCSY and GHSQC experiments were performed using the standard pulse sequences available with the Varian INOVA 500 system. Unless otherwise stated the value for the chemical shift is given to the centre of the multiplet. The multiplets in the ^{1}H NMR spectra have been described in terms of their two- and three-bond coupling, with splitting due to longer bond coupling being ignored. The ^{1}H NMR spectra for the ligands are denoted with primes to distinguish between the different aromatic rings on the ligands.

Electrospray (ES) mass spectra were recorded using a Micromass LCT-TOF mass spectrometer, with a probe operating at 3200V and a cone voltage of 30V. Samples were dissolved in 1:1 acetonitrile:water, and spectra acquired using source and desolvation temperatures of 80°C and 150°C respectively.

Melting points were recorded on a Electrochemical melting point apparatus and are uncorrected. Elemental analyses were performed by the Campbell microanalytical laboratory, University of Otago, Dunedin.

Unless otherwise stated, reagents were obtained from commercial sources and used as supplied. Solvents were purified by standard literature procedures and freshly distilled as required. The following compounds were prepared by literature procedures: copper(I) iodide,[309] 2-chloroquinoxaline.[310]

Preparation of ligands

General procedure for the preparation of the poly(heteroaryloxy)-substituted ligands.

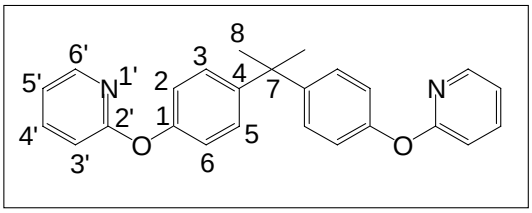
The synthesis adopted to make these ligands was analogous to that of O'Keefe et al.[112] A mixture of the Bisphenol (1 equiv.) and potassium carbonate (approx. 2 equiv. per hydroxyl) was stirred in a solution of sulpholane/toluene (10ml:5ml) at room temperature under argon for 45 minutes. The haloheterocycle (2-bromopyridine, 2-chloroquinoline, 2-chloropyrazine, 2-chloroquinoxaline) (1 equiv per hydroxyl) was quickly added to this solution. The mixture was heated to reflux at ~180°C under argon for 48 hours. After 48 hours the resulting mixture was poured into a solution of 10% aqueous sodium hydroxide solution (~20ml) and water (~10ml). This was then extracted with chloroform. The chloroform extracts were combined and reduced *in vacuo* to give the crude product in a sulpholane solution. The resulting sulpholane solution was added to acetone, heated, treated with decolourising charcoal and filtered. The acetone was removed *in vacuo* to give the crude product saturated in the sulpholane solution. Just enough water was added to the sulpholane solution to precipitate the crude product, which was subsequently redissolved in acetone. Recrystallisation from this acetone/water solution gave the pure product.

General procedure for the preparation of the poly(pyridylmethoxy)-substituted ligands.

The synthesis adopted to make these ligands was analogous to that of Hartshorn et al.[102, 172] A mixture of the Bisphenol, the appropriate chloromethylpyridine.HCl (approx. 1 equiv. per hydroxyl group) and 40% aqueous tetrabutylammonium hydroxide ('6 drops') was refluxed (~80°C) in 25ml benzene and 7ml 40% aqueous sodium hydroxide solution for 48 hours. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give a crude solid or oil, which was then purified by recrystallisation or column chromatography.

Preparation of the Bisphenol A based ligands

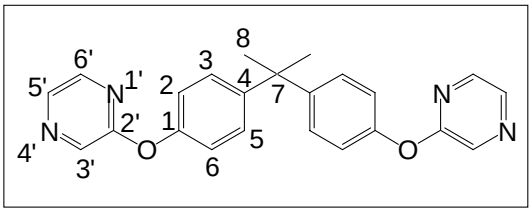
2,2-Di(4-(2-pyridyloxy)phenyl)propane, **2.19**



A mixture of Bisphenol A (1.617g, 7.08mmol) and potassium carbonate (3.95g, 28.58mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Bromopyridine (2.23g, 14.1mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x50mls). Recrystallisation from acetone/water gave **2.19** as a white solid. Yield 2.204g (81.8%). M.p. 110-113°C. Anal. Found: C, 78.16; H, 5.86; N, 7.16. Calc. for $C_{25}H_{22}N_2O_2$: C, 78.51; H, 5.80; N, 7.32. ^{1}H NMR (300MHz, $CHCl_3$): δ 8.21 (2H, d, H6'), 7.66 (2H, t, H4'), 7.29 (4H, d, H3, H5), 7.04 (4H, d, H2, H6), 6.98 (2H, t, H5'), 6.88 (2H, d, H3'), 1.71 (6H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 163.67, 151.96, 147.69, 146.62, 139.42, 128.08, 120.31, 118.37, 111.52, 42.29, 30.96. ESI-MS: Found MH^+ = 383.1763; $C_{25}H_{23}N_2O_2$ requires MH^+ = 383.1760.

Colourless crystals suitable for X-ray crystallography were prepared by slow evaporation of an acetone solution of the ligand.

2,2-Di(4-(2-pyrazinyloxy)phenyl)propane, **2.21**

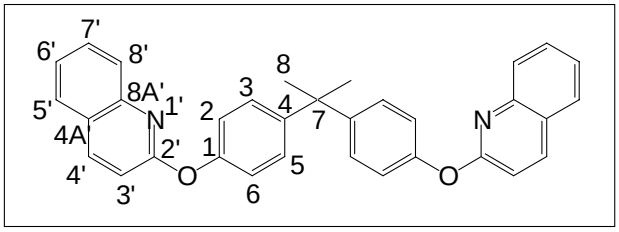


A mixture of Bisphenol A (1.608g, 7.04mmol) and potassium carbonate (4.00g, 28.9mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. Chloropyrazine (1.613g, 14.1mmol) was then quickly added to this solution and the mixture was heated to reflux (~130°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x50mls). Recrystallisation from acetone/water gave **2.21** as a white crystalline solid. Yield 2.11g (78%). M.p. 130°C. Anal. Found: C, 71.73; H, 5.31; N, 14.72. Calc. for $C_{23}H_{20}N_4O_2$: C, 71.86; H, 5.24; N, 14.57. ^{1}H

NMR (300MHz, $CHCl_3$): δ 8.41 (2H, s, H3'), 8.27 (2H, s, H6'), 8.13 (2H, s, H5'), 7.30 (4H, d, H3,H5), 7.08 (4H, d, H2,H6), 1.73 (6H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 160.11, 150.86, 147.33, 141.08, 138.33, 135.85, 128.17, 120.46, 42.41, 30.90. ESI-MS: Found MH^+ = 385.1648; $C_{23}H_{21}N_4O_2$ requires MH^+ = 385.1665.

Pale yellow block crystals suitable for X-ray crystallography were prepared by slow evaporation of an acetone solution of the ligand.

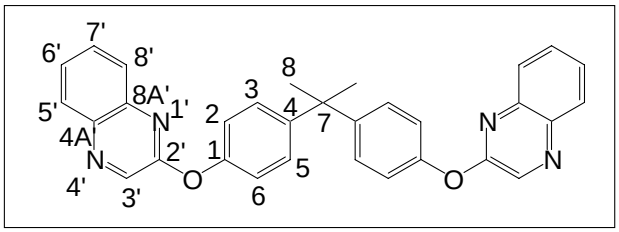
2,2-Di(4-(2-quinolyloxy)phenyl)propane, **2.23**



A mixture of Bisphenol A (0.402g, 1.76mmol) and potassium carbonate (0.987g, 7.14mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Chloroquinoline (0.581g, 3.55mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x50mls). Recrystallisation from acetone/water gave **2.23** as a white solid. Yield 0.602g (70.8%). M.p. 236-238°C. Anal. Found: C, 77.52; H, 5.25; N, 5.47. Calc. for $C_{33}H_{26}N_2O_2.1½H_2O$: C, 77.78; H, 5.74; N, 5.50. ^1H NMR (300MHz, $CHCl_3$): δ 8.13 (2H, d, H4'), 8.10 (2H, d, H8'), 7.83 (2H, d, H5'), 7.76 (2H, t, H7'), 7.62 (2H, t, H6'), 7.44 (4H, d, H3,H5), 7.30 (4H, d, H2,H6), 7.08 (2H, d, H3'), 1.66 (6H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 161.62, 151.67, 146.82, 146.42, 139.75, 129.75, 127.97, 127.89, 127.31, 125.64, 124.79, 120.57, 112.68, 42.40, 31.05. ESI-MS: Found MH^+ = 483.2049; $C_{33}H_{27}N_2O_2$ requires MH^+ = 483.2073.

Pale yellow crystals suitable for X-ray crystallography were obtained by slow evaporation of a dichloromethane solution of the ligand.

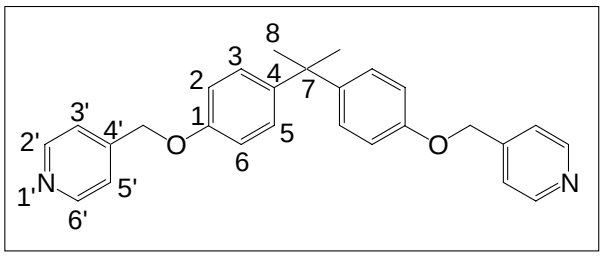
2,2-Di(4-(2-quinoxalinyloxy)phenyl)propane, **2.25**



A mixture of Bisphenol A (0.805g, 3.55mmol) and potassium carbonate (1.965g, 14.22mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Chloroquinoxaline (1.160g, 7.05mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x80mls). Recrystallisation from acetone/water gave **2.25** as a yellow crystalline solid. Yield 1.703g (99.7%). M.p.181-182°C. Anal. Found: C, 76.84; H, 5.17; N, 11.48. Calc. for $C_{31}H_{24}N_4O_2$: C, 76.84; H, 4.99; N, 11.56. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.69 (2H, s, H3'), 8.06 (2H, d, H8'), 7.79 (2H, d, H5'), 7.67 (4H, m, H6',H7'), 7.37 (4H, d, H3,H5), 7.23 (4H, d, H2,H6), 1.77 (6H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.82, 150.63, 147.42, 139.96, 139.48, 139.19, 130.33, 128.83, 128.04, 127.69, 127.39, 120.62, 42.50, 30.99. ESI-MS: Found MH^+ = 485.1991; $C_{31}H_{25}N_4O_2$ requires MH^+ = 485.1978.

Yellow crystals suitable for X-ray crystallography were obtained by slow evaporation of a dichloromethane/methanol solution of the ligand.

2,2-Di(4-(4-pyridylmethoxy)phenyl)propane, **2.45**

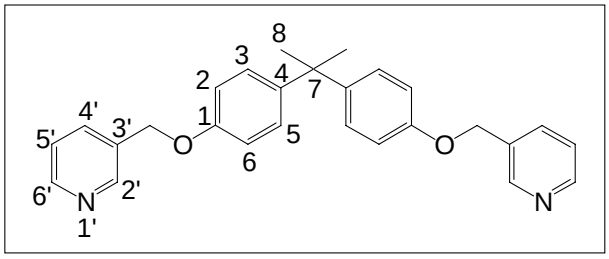


A mixture of Bisphenol A (1.062g, 4.65mmol) 4-chloromethylpyridine.HCl (1.532g, 9.3mmol) and 40% aqueous tetrabutylammonium hydroxide (6 drops) was refluxed (~80°C) in 20ml of benzene and 5ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **2.45** as an orange oil that solidified on standing. Recrystallisation from ethyl acetate/petroleum ether (1:10) gave **2.45** as a yellow solid. Yield 0.737g (38.6%). M.p. 135-136°C. Anal. Found: C, 78.88; H, 6.48; N, 6.86. Calc for $C_{27}H_{26}N_2O_2$: C, 79.00; H, 6.38; N, 6.82. ^{1}H NMR (300MHz, $CHCl_3$): δ

8.62 (4H, d, H2',H6'), 7.36 (4H, d, H3',H5'), 7.15 (4H, d, H3,H5), 6.85 (4H, d, H2,H6), 5.06 (4H, s, CH_2), 1.63 (6H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 155.97, 149.46, 147.00, 143.85, 127.86, 121.62, 114.13, 68.08, 41.75, 30.96. ESI-MS: Found MH^+ = 411.2092; $C_{27}H_{27}N_2O_2$ requires MH^+ = 411.2073.

Colourless crystals suitable for X-ray crystallography were obtained by slow evaporation of an acetonitrile solution of the ligand.

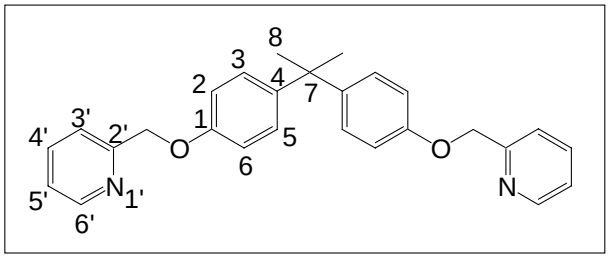
2,2-Di(4-(3-pyridylmethoxy)phenyl)propane, **2.47**



A mixture of Bisphenol A (1.095g, 4.8mmol) 3-chloromethylpyridine.HCl (1.680g, 10.24mmol) and 40% aqueous tetrabutylammonium hydroxide (6 drops) was refluxed (~80°C) in 20ml of benzene and 5ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **2.47** as an orange oil that solidified on standing. Recrystallisation from ethyl acetate/petroleum ether (1:10) gave **2.47** as a yellow solid. Yield 1.04g (52.9%). M.p. 127-128.5°C. Anal. Found: C, 78.74; H, 6.43; N, 6.79. Calc for $C_{27}H_{26}N_2O_2$: C, 79.00; H, 6.38; N, 6.82. ^1H NMR (300MHz, $CHCl_3$): δ 8.67 (2H, s, H2'), 8.58 (2H, d, H6'), 7.77 (2H, d, H4'), 7.31 (2H, m, H5'), 7.16 (4H, d, H3,H5), 6.88 (4H, d, H2,H6), 5.04 (4H, s, CH_2), 1.64 (6H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.20, 149.22, 148.83, 143.72, 135.36, 132.73, 127.81, 123.51, 114.11, 67.45, 41.72, 30.97. ESI-MS: Found MH^+ = 411.2059; $C_{27}H_{27}N_2O_2$ requires MH^+ = 411.2073.

Colourless crystals suitable for X-ray crystallography were grown from a solution of the ligand and $Cd(NO_3)_2$ in methanol.

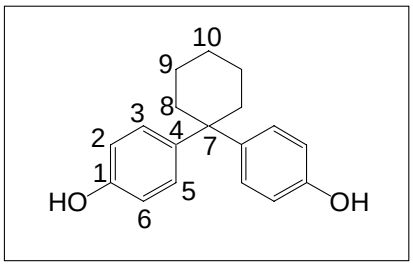
2,2-Di(4-(2-pyridylmethoxy)phenyl)propane, **2.49**



A mixture of Bisphenol A (1.084g, 4.75mmol) 2-chloromethylpyridine.HCl (1.558g, 9.5mmol) and 40% aqueous tetrabutylammonium hydroxide (6 drops) was refluxed (~80°C) in 20ml of benzene and 5ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **2.49** as an orange oil that solidified on standing. Recrystallisation from ethyl acetate/petroleum ether (1:10) gave **2.49** as a white solid. Yield 0.507g (26%). M.p. 71-72°C. Anal. Found: C, 78.73; H, 6.51; N, 6.85. Calc for $C_{27}H_{26}N_2O_2$: C, 79.00; H, 6.38; N, 6.82. ^{1}H NMR (300MHz, $CHCl_3$): δ 8.59 (2H, d, H6'), 7.72 (2H, t, H4'), 7.69 (2H, d, H3'), 7.22 (2H, m, H5'), 7.15 (4H, d, H3,H5), 6.88 (4H, d, H2,H6), 5.18 (4H, s, CH_2), 1.63 (6H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 157.46, 156.22, 149.11, 143.52, 136.79, 127.77, 122.52, 121.21, 114.12, 70.56, 41.68, 30.98. ESI-MS: Found MH^+ = 411.2076; $C_{27}H_{27}N_2O_2$ requires MH^+ = 411.2073.

Preparation of the Bisphenol Z based ligands

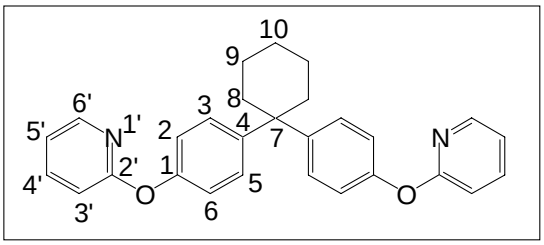
Preparation of Bisphenol Z, **2.52**



The synthesis adopted to make Bisphenol Z was adapted from a paper by Kolasa et al. using a similar procedure.[176] A mixture of cyclohexanone (1.737g, 17.7mmol) and phenol (5.64g, 60.0mmol) in 1,4-dioxane (10ml) and water (10ml) was stirred at 0°C. At 0°C 20ml of concentrated H_2SO_4 was added dropwise. The mixture went a deep orange/red colour on addition of the H_2SO_4. The mixture was warmed to room temperature and then stirred for 24 hours. The resulting mixture was poured onto 50ml ice-water and extracted with ethyl acetate (3x80mls). The ethyl acetate layers were combined and washed with water and brine, dried over $MgSO_4$ and reduced *in vacuo* to an orange/purple solid. Flash chromatography (20g silica, 20:80 petroleum ether/ethyl acetate) gave **2.52** as a yellow solid. Yield 1.80g (37.9%). M.p. 180-183°C (lit.[311] 190-192°C). ^{1}H NMR (300MHz,

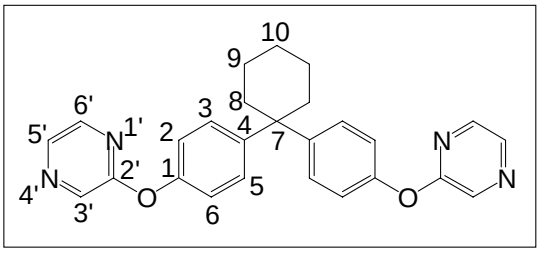
DMSO): δ 9.21 (2H, s, OH), 7.12 (4H, d, H3,H5), 6.72 (4H, d, H2,H6), 2.21 (4H, m, H8), 1.51 (6H, m, H9,H10).

1,1-Di(4-(2-pyridyloxy)phenyl)cyclohexane, **2.53**



A mixture of Bisphenol Z (1.986g, 7.4mmol) and potassium carbonate (4.09g, 29.6mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Bromopyridine (2.33g, 14.7mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x50mls). Recrystallisation from acetone/water gave **2.53** as a white solid. Yield 2.18g (69.8%). M.p. 97-98°C. Anal. Found: C, 79.61; H, 6.27; N, 6.57. Calc. for $C_{28}H_{26}N_2O_2$: C, 79.59; H, 6.20; N, 6.63. ^{1}H NMR (300MHz, $CHCl_3$): δ 8.20 (2H, d, H6'), 7.66 (2H, t, H4'), 7.30 (2H, d, H3,H5), 7.05 (2H, d, H2,H6), 6.97 (2H, t, H5'), 6.86 (2H, d, H3'), 2.28 (4H, m, H8), 1.58 (4H, m, H9), 1.51 (2H, m, H10). ^{13}C NMR (75MHz, $CDCl_3$): δ 163.62, 151.77, 147.68, 144.57, 139.44, 128.43, 120.41, 118.40, 111.52, 45.55, 37.30, 26.32, 22.81. ESI-MS: Found MH^+ = 423.2065; $C_{28}H_{27}N_2O_2$ requires MH^+ = 423.2073.

1,1-Di(4-(2-pyrazinyloxy)phenyl)cyclohexane, **2.54**

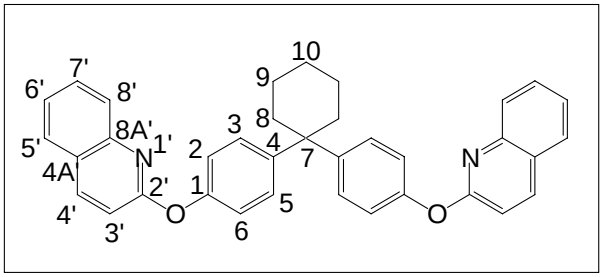


A mixture of Bisphenol Z (1.896g, 7.06mmol) and potassium carbonate (3.96g, 28.65mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. Chloropyrazine (1.623g, 14.2mmol) was then quickly added to this solution and the mixture was heated to reflux (~130°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x50mls). Recrystallisation from

acetone/water gave **2.54** as a white crystalline solid. Yield 2.46g (82.1%). M.p. 132-134°C. Anal. Found: C, 73.62; H, 5.76; N, 13.16. Calc. for $C_{26}H_{24}N_4O_2$: C, 73.56; H, 5.70; N, 13.20. ^{1}H NMR (300MHz, $CHCl_3$): δ 8.38 (2H, s, H3'), 8.25 (2H, s, H6'), 8.10 (2H, s, H5'), 7.33 (4H, d, H3,H5), 7.08 (4H, s, H2,H6), 2.30 (4H, m, H8), 1.59 (4H, m, H9), 1.52 (2H, m, H10). ^{13}C NMR (75MHz, $CDCl_3$): δ 160.10, 150.67, 145.26, 141.08, 138.34, 135.82, 128.51, 120.57, 45.65, 37.25, 26.23, 22.76. ESI-MS: Found MH^+ = 425.1981; $C_{26}H_{25}N_4O_2$ requires MH^+ = 425.1978.

Yellow crystals suitable for X-ray crystallography were obtained by slow evaporation of the mother liquor from the recrystallisation.

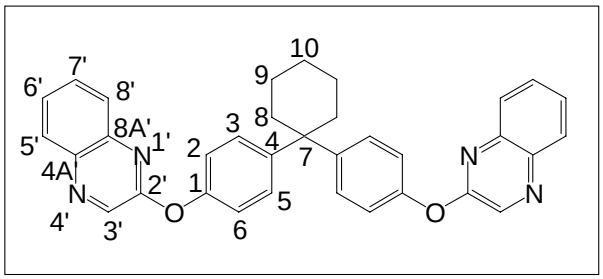
1,1-Di(4-(2-quinolyloxy)phenyl)cyclohexane, **2.55**



A mixture of Bisphenol Z (0.475g, 1.77mmol) and potassium carbonate (1.02g, 7.38mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. The 2-chloroquinoline (0.579g, 3.54mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x60mls). Recrystallisation from acetone/water gave **2.55** as a yellow crystalline solid. Yield 0.69g (74.6%). M.p. 174-176°C. Anal. Found: C, 80.03; H, 6.21; N, 4.88. Calc. for $C_{36}H_{30}N_2O_2.½H_2O$: C, 80.33; H, 6.11; N, 5.00. ^{1}H NMR (300MHz, $CHCl_3$): δ 8.10 (2H, d, H4'), 7.83 (2H, d, H8'), 7.75 (2H, d, H5'), 7.61 (2H, t, H7'), 7.43 (2H, t, H6'), 7.37 (4H, d, H3,H5), 7.19 (4H, d, H2,H6), 7.06 (2H, d, H3'), 2.34 (4H, m, H8), 1.63 (4H, m, H9), 1.55 (2H, m, H10). ^{13}C NMR (75MHz, $CDCl_3$): δ 161.61, 151.46, 146.42, 144.77, 139.74, 129.74, 128.33, 127.87, 127.31, 125.64, 124.79, 120.75, 112.68, 45.67, 37.67, 26.38, 22.88. ESI-MS: Found MH^+ = 523.2390; $C_{36}H_{31}N_2O_2$ requires MH^+ = 523.2386.

Yellow crystals suitable for X-ray crystallography were obtained out from the mother liquor of the recrystallisation.

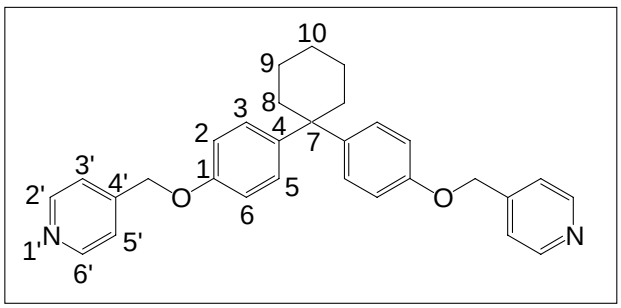
1,1-Di(4-(2-quinoxalinyloxy)phenyl)cyclohexane, **2.56**



A mixture of Bisphenol Z (0.477g, 1.78mmol) and potassium carbonate (0.984g, 7.12mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. The 2-chloroquinoxaline (0.580g, 3.524mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (4x80mls). Recrystallisation from acetone/water gave **2.56** as a yellow solid. Yield 0.495g (53.4%). M.p. 161-162°C. Anal. Found: C, 76.15; H, 5.62; N, 10.10. Calc. for $C_{34}H_{28}N_4O_2.½H_2O$: C, 76.53; H, 5.48; N, 10.50. ^{1}H NMR (300MHz, $CHCl_3$): δ 8.66 (2H, s, H3'), 8.06 (2H, d, H8'), 7.80 (2H, d, H5'), 7.62 (4H, m, H6',H7'), 7.40 (4H, d, H3,H5), 7.25 (4H, d, H2,H6), 2.35 (4H, m, H8), 1.64 (4H, m, H9), 1.56 (2H, m, H10). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.80, 150.45, 145.39, 139.96, 139.56, 139.27, 130.32, 128.87, 128.42, 127.72, 127.39, 120.78, 45.78, 37.36, 26.32, 22.85. ESI-MS: Found MH^+ = 525.2309; $C_{34}H_{29}N_4O_2$ requires MH^+ = 525.2291.

Colourless crystals suitable for X-ray crystallography were grown from a solution of the ligand and $ZnCl_2$ in methanol.

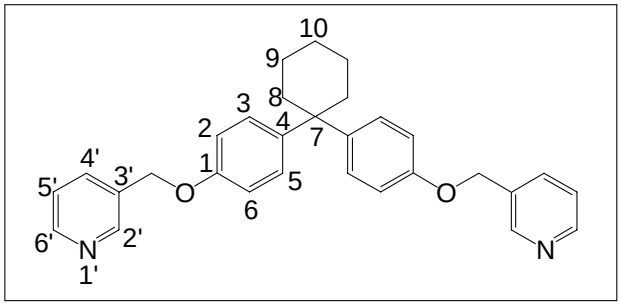
1,1-Di(4-(4-pyridylmethoxy)phenyl)cyclohexane, **2.67**



A mixture of Bisphenol Z (1.246g, 4.64mmol) 4-chloromethylpyridine.HCl (1.538g, 9.4mmol) and 40% aqueous tetrabutylammonium hydroxide (6 drops) was refluxed (~80°C) in 20ml of benzene and 5ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **2.67** as a brown viscous oil. Flash chromatography (20g

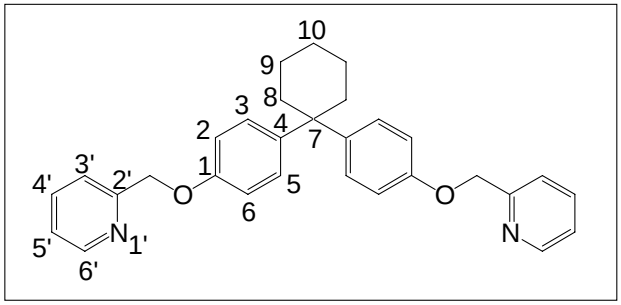
silica, 40:60 petroleum ether/ethyl acetate) gave **2.67** as a white crystalline solid. Yield 0.30g (14.4%). M.p. 130-132°C. Anal. Found: C, 79.70; H, 6.80; N, 6.18. Calc for $C_{30}H_{30}N_2O_2$: C, 79.97; H, 6.71; N, 6.22. ^{1}H NMR (300MHz, $CHCl_3$): δ 8.59 (4H, s, H2',H6'), 7.33 (4H, d, H3',H5'), 7.18 (4H, d, H3,H5), 6.85 (4H, d, H2,H6), 5.02 (4H, s, CH_2), 2.21 (4H, m, H8), 1.52 (6H, m, H9,H10). ^{13}C NMR (75MHz, $CDCl_3$): δ 155.74, 149.66, 146.65, 141.74, 128.17, 121.52, 114.31, 68.03, 45.03, 37.27, 26.29, 22.81. ESI-MS: Found MH^+ = 451.2381; $C_{30}H_{31}N_2O_2$ requires MH^+ = 451.2386.

1,1-Di(4-(3-pyridylmethoxy)phenyl)cyclohexane, **2.68**



A mixture of Bisphenol Z (1.223g, 4.56mmol) 3-chloromethylpyridine.HCl (1.602g, 9.8mmol) and 40% aqueous tetrabutylammonium hydroxide (6 drops) was refluxed (~80°C) in 20ml of benzene and 5ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **2.68** as an orange oil that solidified on standing. Recrystallisation from ethyl acetate/petroleum ether (1:10) gave **2.68** as an orange solid. Yield 0.335g (16.3%). M.p. 117-118°C. Anal. Found: C, 79.90; H, 6.78; N, 6.25. Calc for $C_{30}H_{30}N_2O_2$: C, 79.97; H, 6.71; N, 6.22. ^{1}H NMR (300MHz, $CHCl_3$): δ 8.66 (2H, s, H2'), 8.57 (2H, s, H6'), 7.76 (2H, d, H4'), 7.32 (2H, m, H5'), 7.17 (4H, d, H3,H5), 6.89 (4H, d, H2,H6), 5.03 (4H, s, CH_2), 2.22 (4H, m, H8), 1.53 (6H, m, H9,H10). ^{13}C NMR (75MHz, $CDCl_3$): δ 155.97, 149.13, 148.74, 141.69, 135.47, 132.81, 128.19, 123.56, 114.33, 67.40, 45.08, 37.32, 26.34, 22.86. ESI-MS: Found MH^+ = 451.2365; $C_{30}H_{31}N_2O_2$ requires MH^+ = 451.2386.

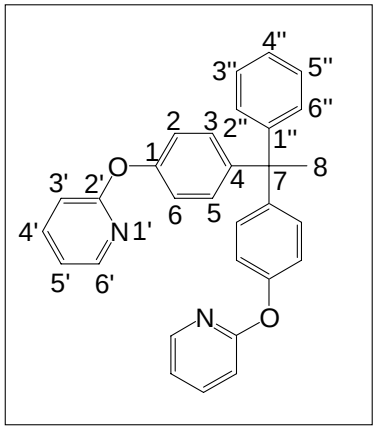
1,1-Di(4-(2-pyridylmethoxy)phenyl)cyclohexane, **2.69**



A mixture of Bisphenol Z (1.267g, 4.72mmol) 2-chloromethylpyridine.HCl (1.542g, 9.4mmol) and 40% aqueous tetrabutylammonium hydroxide (6 drops) was refluxed (~80°C) in 20ml of benzene and 5ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **2.69** as an orange oil that solidified on standing. Recrystallisation from ethyl acetate/petroleum ether (1:10) gave **2.69** as a white solid. Yield 0.947g (44.6%). M.p. 98-99.5°C. Anal. Found: C, 79.95; H, 6.72; N, 6.22. Calc for $C_{30}H_{30}N_2O_2$: C, 79.97; H, 6.71; N, 6.22. ^{1}H NMR (300MHz, $CHCl_3$): δ 8.56 (2H, d, H6'), 7.69 (2H, t, H4'), 7.52 (2H, d, H3'), 7.20 (2H, m, H5'), 7.16 (4H, d, H3,H5), 6.89 (4H, d, H2,H6), 5.16 (4H, s, CH_2), 2.19 (4H, m, H8), 1.50 (6H, m, H9,H10). ^{13}C NMR (75MHz, $CDCl_3$): δ 157.27, 155.91, 148.60, 141.54, 137.30, 128.16, 122.67, 121.43, 114.35, 70.19, 45.05, 37.33, 26.37, 22.87. ESI-MS: Found MH^+ = 451.2364; $C_{30}H_{31}N_2O_2$ requires MH^+ = 451.2386.

Preparation of the Bisphenol AP based ligands

1,1-Di(4-(2-pyridyloxy)phenyl)phenylethane, **3.2**

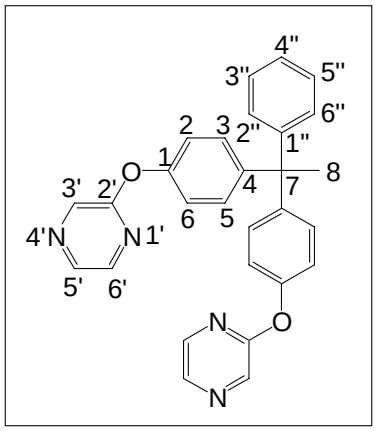


A mixture of Bisphenol AP (2.04g, 7.03mmol) and potassium carbonate (4.01g, 29.0mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Bromopyridine (2.31g, 14.6mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x50mls). Recrystallisation from acetone/water gave **3.2** as a white crystalline solid. Yield 2.61g (83.6%). M.p. 108-111°C. Anal. Found: C, 80.73; H, 5.51; N, 6.30. Calc. for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30. ^{1}H NMR

(500MHz, $CHCl_3$): δ 8.20 (2H, d, H6'), 7.67 (2H, t, H4'), 7.27 (2H, t, H3",H5"), 7.20 (1H, t, H4"), 7.18 (6H, m, H2",H6",H3,H5), 7.13 (4H, d, H2,H6), 7.03 (2H, t, H5'), 6.97 (2H, d, H3'), 2.19 (3H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 163.50, 152.28, 148.91, 147.68, 145.02, 139.47, 129.97, 128.68, 127.88, 126.02, 120.03, 118.51, 111.65, 51.79, 30.67. ESI-MS: Found MH^+ = 445.1894; $C_{30}H_{25}N_2O_2$ requires MH^+ = 445.1916.

Colourless crystals suitable for X-ray crystallography were obtained by slow evaporation of an acetone solution of the ligand.

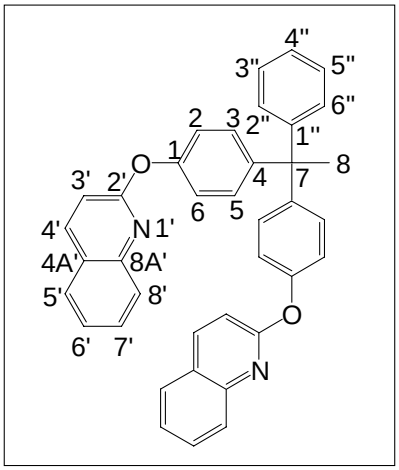
1,1-Di(4-(2-pyrazinyloxy)phenyl)phenylethane, **3.3**



A mixture of Bisphenol AP (1.022g, 3.52mmol) and potassium carbonate (2.03g, 14.7mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. Chloropyrazine (0.807g, 7.05mmol) was then quickly added to this solution and the mixture was heated to reflux (~130°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x60mls). Recrystallisation from acetone/water gave **3.3** as a white crystalline solid. Yield 1.53g (97.3%). M.p.151-155°C. Anal. Found: C, 74.93; H, 5.11; N, 12.65. Calc. for $C_{28}H_{22}N_4O_2$: C, 75.32; H, 4.97; N, 12.55. ^1H NMR (500MHz, $CHCl_3$): δ 8.41 (2H, s, H3'), 8.26 (2H, d, H6'), 8.11 (2H, m, H5'), 7.30 (2H, t, H3",H5"), 7.22 (1H, t, H4"), 7.16 (6H, m, H2",H6",H3,H5), 7.07 (4H, d, H2,H6), 2.22 (3H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 160.02, 151.19, 148.55, 145.79, 141.09, 138.50, 135.93, 130.07, 128.62, 127.99, 126.18, 120.27, 51.89, 30.66. ESI-MS: Found MH^+ = 447.1838; $C_{28}H_{23}N_4O_2$ requires MH^+ = 447.1821.

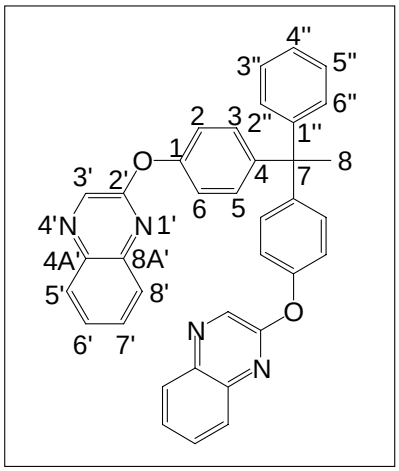
Colourless crystals suitable for X-ray crystallography were grown from a solution of the ligand and $ZnBr_2$ in methanol.

1,1-Di(4-(2-quinolyloxy)phenyl)phenylethane, **3.4**



A mixture of Bisphenol AP (1.019g, 3.51mmol) and potassium carbonate (1.849g, 13.4mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Chloroquinoline (1.161g, 7.10mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (4x60mls). Recrystallisation from acetone/water gave **3.4** as a yellow crystalline solid. Yield 1.309g (68.7%). M.p. 180°C. Anal. Found: C, 82.19; H, 5.25; N, 4.98. Calc. for $C_{38}H_{28}N_2O_2.½H_2O$: C, 82.44; H, 5.28; N, 5.06. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.07 (2H, d, H4'), 7.82 (2H, d, H8'), 7.73 (2H, d, H5'), 7.59 (2H, t, H7'), 7.39 (2H, t, H6'), 7.30 (2H, t, H3",H5"), 7.22 (7H, m, H2",H4",H6",H3,H5), 7.07 (4H, d, H2,H6), 2.24 (3H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 161.48, 151.95, 149.02, 146.35, 145.24, 139.81, 129.87, 129.80, 128.73, 127.94, 127.84, 127.33, 126.07, 125.66, 124.85, 120.39, 112.72, 51.89, 30.77. ESI-MS: Found MH^+ = 545.2239; $C_{38}H_{29}N_2O_2$ requires MH^+ = 545.2229.

1,1-Di(4-(2-quinoxalinyloxy)phenyl)phenylethane, **3.5**

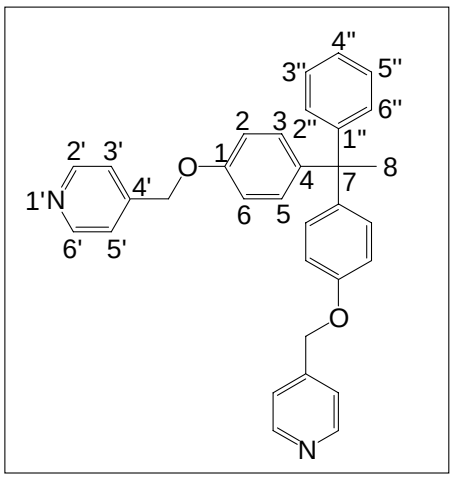


A mixture of Bisphenol AP (0.511g, 1.76mmol) and potassium carbonate (0.978g, 7.08mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Chloroquinoline (0.581g, 3.53mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x80mls). Recrystallisation from acetone/water gave **3.5** as a yellow crystalline solid. Yield 0.604g (59.6%). M.p.136.5°C. Anal. Found: C, 76.77; H, 5.00; N, 9.08. Calc. for

$C_{36}H_{27}N_4O_2.⅓H_2O.CH_3COCH_3$: C, 76.70; H, 5.39; N, 9.17. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.69 (2H, d, H3'), 8.07 (2H, d, H8'), 7.80 (2H, d, H5'), 7.68 (2H, t, H6'), 7.63 (2H, t, H7'), 7.34 (2H, t, H3",H5"), 7.27-7.14 (11H, m, H2,H3,H5,H6,H2",H4",H6"), 2.28 (3H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.77, 150.93, 148.72, 145.94, 139.91, 139.09, 130.45, 129.97, 128.81, 128.69, 128.04, 127.73, 127.54, 126.22, 120.49, 104.70, 51.13, 22.78. ESI-MS: Found MH^+ = 547.2112; $C_{36}H_{27}N_4O_2$ requires MH^+ = 547.2134.

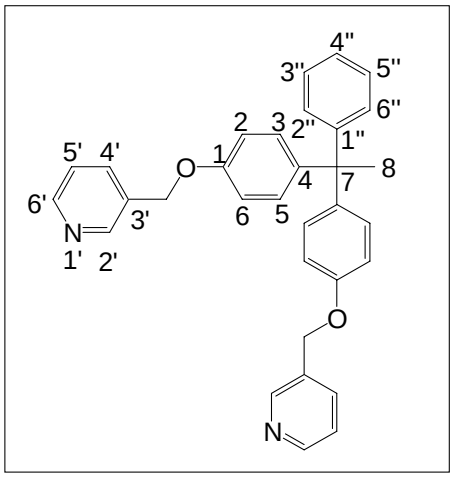
Yellow crystals suitable for X-ray crystallography were grown from a solution of the ligand in dichloromethane and $ZnCl_2$ in methanol.

1,1-Di(4-(4-pyridylmethoxy)phenyl)phenylethane, **3.9**



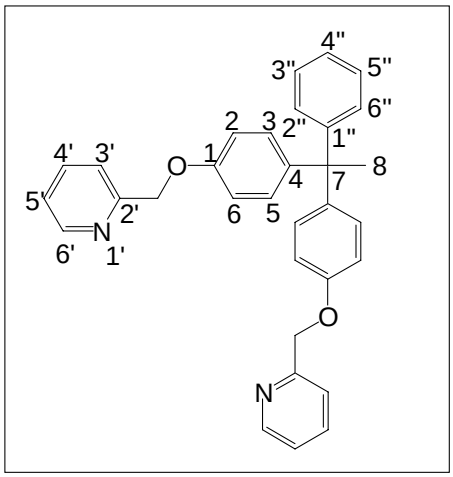
A mixture of Bisphenol AP (1.259g, 4.34mmol) 4-chloromethylpyridine.HCl (1.671g, 10.18mmol) and 40% aqueous tetrabutylammonium hydroxide (6 drops) was refluxed (~80°C) in 20ml of benzene and 6ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **3.9** as a orange/brown oil that solidified on standing. Recrystallisation from ethyl acetate/petroleum ether (1:10) gave **3.9** as a brown solid. Yield 0.986g (48.1%). M.p. 124°C. Anal. Found: C, 80.34; H, 6.18; N, 6.04 Calc for $C_{32}H_{28}N_2O_2.⅓H_2O$: C, 80.31; H, 6.04; N, 5.85. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.61 (4H, d, H2',H6'), 7.35 (4H, d, H3',H5'), 7.27 (2H, t, H3",H5"), 7.21 (1H, m, H4"), 7.19 (2H, d, H2",H6"), 7.07 (4H, d, H3,H5), 6.84 (4H, d, H2,H6), 5.06 (4H, s, CH_2), 2.13 (3H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.20, 149.84, 149.22, 146.31, 142.16, 129.74, 128.48, 127.81, 125.90, 121.47, 113.92, 68.05, 51.23, 30.58. ESI-MS: Found MH^+ = 473.2234; $C_{32}H_{29}N_2O_2$ requires MH^+ = 473.2229.

1,1-Di(4-(3-pyridylmethoxy)phenyl)phenylethane, **3.10**



A mixture of Bisphenol AP (1.352g, 4.66mmol) 3-chloromethylpyridine.HCl (1.530g, 9.30mmol) and 40% aqueous tetrabutylammonium hydroxide (6 drops) was refluxed (~80°C) in 20ml of benzene and 6ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **3.10** as a brown oil that solidified on standing. Attempted crystallisation from ethyl acetate/petroleum ether (1:10) gave a brown oil that solidified on standing. Yield 1.80g (81.8%). M.p. 98-99°C. Anal. Found: C, 80.63; H, 6.22; N, 5.84 Calc for $C_{32}H_{28}N_2O_2.⅓H_2O$: C, 80.31; H, 6.04; N, 5.85. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.66 (2H, s, H2'), 8.57 (2H, d, H6'), 7.76 (2H, d, H4'), 7.30 (2H, t, H5'), 7.26 (2H, t, H3",H5"), 7.20 (1H, t, H4"), 7.09 (2H, d, H2",H6"), 7.01 (4H, d, H3,H5), 6.86 (4H, d, H2,H6), 5.03 (4H, s, CH_2), 2.13 (3H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.37, 149.25, 148.84, 142.04, 135.25, 132.54, 129.75, 129.69, 128.46, 127.77, 125.83, 123.44, 113.88, 67.38, 51.19, 30.57. ESI-MS: Found MH^+ = 473.2207; $C_{32}H_{29}N_2O_2$ requires MH^+ = 473.2229.

1,1-Di(4-(2-pyridylmethoxy)phenyl)phenylethane, **3.11**

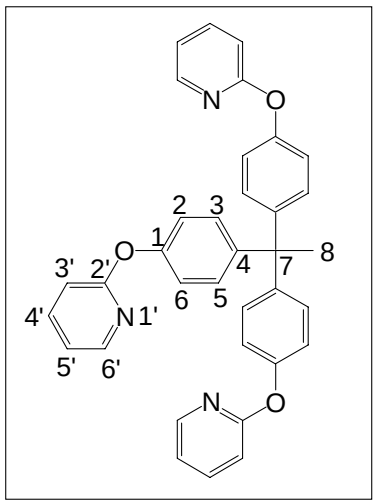


A mixture of Bisphenol AP (1.346g, 4.64mmol) 2-chloromethylpyridine.HCl (1.72g, 10.49mmol) and 40% aqueous tetrabutylammonium hydroxide (6 drops) was refluxed (~80°C) in 20ml of benzene and 6ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **3.11** as a brown oil. Attempted crystallisation from ethyl acetate/petroleum ether (1:10) gave a brown oil. Yield 2.15g (98.1%). ^{1}H NMR (500MHz, $CHCl_3$): δ 8.54 (2H, d, H6'), 7.65 (2H, t, H4'), 7.50 (2H, d, H3'), 7.22 (2H, t, H5'), 7.15 (1H, t, H4"), 7.08 (4H, d, H2",H3",H5",H6"), 7.00 (4H, d, H3,H5), 6.88

(4H, d, H2,H6), 5.16 (4H, s, CH_2), 2.12 (3H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 157.06, 156.22, 149.21, 148.83, 141.70, 136.62, 129.50, 128.33, 127.58, 125.64, 122.37, 121.05, 113.77, 70.27, 51.01, 30.41. ESI-MS: Found MH^+ = 473.2249; $C_{32}H_{29}N_2O_2$ requires MH^+ = 473.2229.

Preparation of the 1,1,1-tris(4-hydroxyphenyl)ethane based ligands

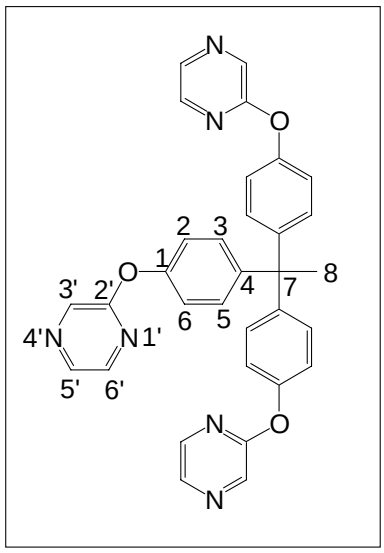
1,1,1-Tris(4-(2-pyridyloxy)phenyl)ethane, **4.15**



A mixture of 1,1,1-tris(4-hydroxyphenyl)ethane (2.161g, 7.05mmol) and potassium carbonate (4.03g, 29.16mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Bromopyridine (3.620g, 22.91mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x50mls). Recrystallisation from acetone/water gave **4.15** as a pale yellow solid. Yield 2.25g (59.4%). M.p. 152-155°C. Anal. Found: C, 78.14; H, 5.21; N, 7.70. Calc. for $C_{35}H_{27}N_3O_3$: C, 78.19; H, 5.06; N, 7.82. ^{1}H NMR (300MHz, $CHCl_3$): δ 8.19 (3H, d, H6'), 7.64 (3H, t, H4'), 7.17 (6H, d, H3,H5), 7.05 (6H, d, H2,H6), 6.96 (3H, t, H5'), 6.89 (3H, d, H3'), 2.19 (3H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 163.47, 152.30, 147.68, 144.93, 139.43, 129.94, 120.05, 118.49, 111.64, 51.43, 30.76. ESI-MS: Found MH^+ = 538.2141; $C_{35}H_{28}N_3O_3$ requires MH^+ = 538.2131.

Colourless crystals suitable for X-ray crystallography were obtained by slow evaporation of a methanol/dichloromethane solution of the ligand.

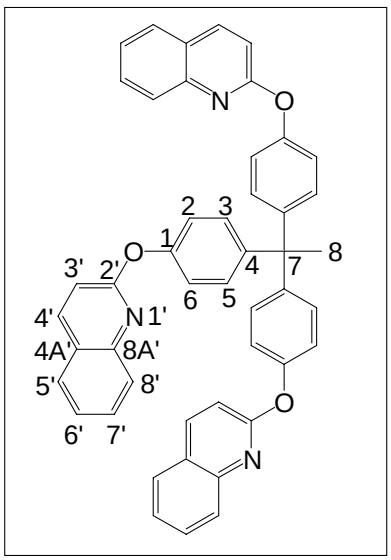
1,1,1-Tris(4-(2-pyrazinyloxy)phenyl)ethane, **4.16**



A mixture of 1,1,1-tris(4-hydroxyphenyl)ethane (0.531g, 1.733mmol) and potassium carbonate (2.192g, 15.86mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. Chloropyrazine (0.697g, 6.08mmol) was then quickly added to this solution and the mixture was heated to reflux (~130°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x80mls). Recrystallisation from acetone/water gave **4.16** as a white crystalline solid. Yield 0.899g (96%). M.p. 178.5°C. Anal. Found: C, 71.16; H, 4.51; N, 15.36. Calc. for $C_{32}H_{24}N_6O_3$: C, 71.10; H, 4.47; N, 15.55. ^{1}H NMR (300MHz, $CHCl_3$): δ 8.42 (3H, s, H3'), 8.28 (3H, s, H6'), 8.27 (3H, s, H5'), 7.21 (6H, d, H3,H5), 7.10 (6H, d, H2,H6), 2.24 (3H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 159.92, 151.25, 145.51, 141.04, 138.48, 135.89, 129.99, 120.33, 51.54, 30.74. ESI-MS: Found MH^+ = 541.1966; $C_{32}H_{25}N_3O_3$ requires MH^+ = 541.1988.

Crystals suitable for X-ray crystallography were obtained by slow evaporation of an acetone solution of the ligand.

1,1,1-Tris(4-(2-quinolyloxy)phenyl)ethane, **4.17**

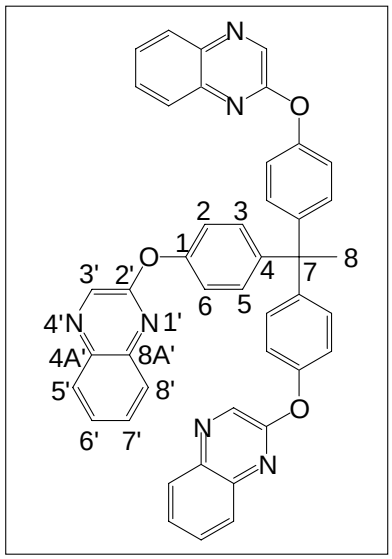


A mixture of 1,1,1-tris(4-hydroxyphenyl)ethane (0.527g, 1.72mmol) and potassium carbonate (2.33g, 16.86mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Chloroquinoline (0.993g, 6.069mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$

(3x60mls). Recrystallisation from acetone/water gave **4.17** as a yellow crystalline solid. Yield 1.157g (97.8%). M.p. 170°C. Anal. Found: C, 80.03; H, 5.26; N, 5.72. Calc. for $C_{47}H_{33}N_3O_3.H_2O$: C, 79.98; H, 5.00; N, 5.95. ^{1}H NMR (300MHz, $CHCl_3$): δ 8.12 (3H, d, H4'), 7.83 (3H, d, H8'), 7.74 (3H, d, H5'), 7.61 (3H, t, H7'), 7.43 (3H, t, H6'), 7.26 (12H, m, H2,H3,H5,H6), 7.08 (3H, d, H3'), 2.28 (3H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 161.49, 152.00, 146.35, 145.23, 139.82, 129.88, 129.80, 127.85, 127.33, 125.66, 124.86, 120.45, 112.73, 51.59, 30.91. ESI-MS: Found MH^+ = 688.2609; $C_{47}H_{34}N_3O_3$ requires MH^+ = 688.2600.

Colourless crystals suitable for X-ray crystallography were grown from a solution of the ligand in dichloromethane and $ZnCl_2$ in methanol.

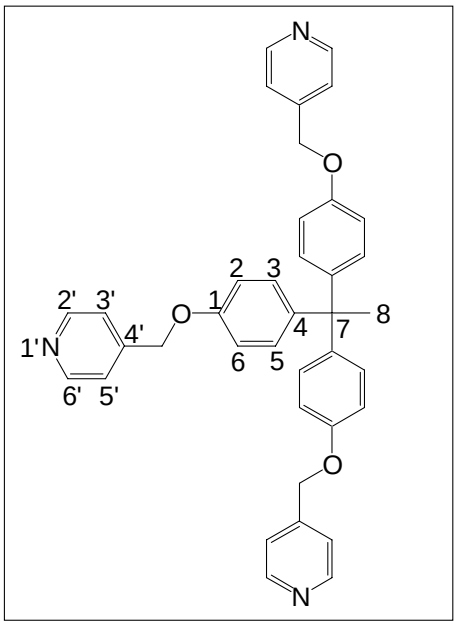
1,1,1-Tris(4-(2-quinoxalinyloxy)phenyl)ethane, **4.18**



A mixture of 1,1,1-tris(4-hydroxyphenyl)ethane (0.530g, 1.73mmol) and potassium carbonate (2.11g, 15.26mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. The 2-chloroquinoxaline (0.991g, 6.02mmol) was then quickly added to this solution and the mixture was heated to reflux (~160°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x80mls). Recrystallisation from acetone/water gave **4.18** as a yellow solid. Yield 0.479g (40.1%). M.p. 160°C. Anal. Found: C, 73.60; H, 4.64; N, 11.13. Calc. for $C_{44}H_{30}N_6O_3.1½H_2O$: C, 73.63; H, 4.63; N, 11.71. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.70 (3H, s, H3'), 8.06 (3H, d, H8'), 7.81 (3H, d, H5'), 7.65 (6H, m, H6',H7'), 7.28 (12H, m, H2,H3,H5,H6), 2.33 (3H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.75, 151.05, 145.74, 139.95, 139.58, 139.23, 130.41, 129.96, 128.90, 127.72, 127.50, 120.60, 51.73, 30.92. ESI-MS: Found MH^+ = 691.2489; $C_{44}H_{31}N_6O_3$ requires MH^+ = 691.2458.

Colourless crystals suitable for X-ray crystallography were grown from a solution of the ligand in dichloromethane and $ZnCl_2$ in methanol.

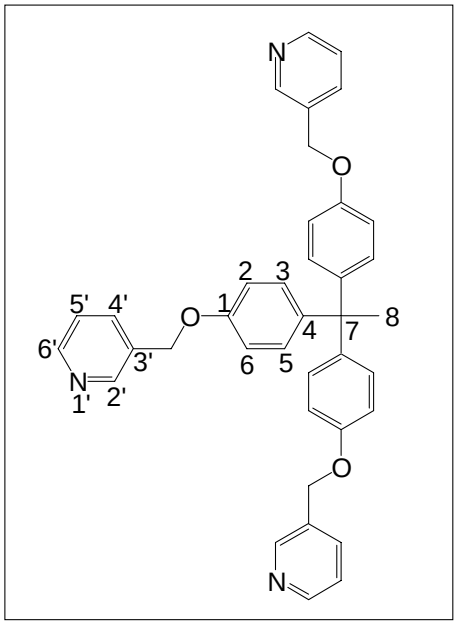
1,1,1-Tris(4-(4-pyridylmethoxy)phenyl)ethane, **4.24**



A mixture of 1,1,1-tris(4-hydroxyphenyl)ethane (1.425g, 4.65mmol) 4-chloromethylpyridine.HCl (2.289g, 13.95mmol) and 40% aqueous tetrabutylammonium hydroxide (6 drops) was refluxed (~80°C) in 25ml of benzene and 7ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **4.24** as an orange solid. Yield 1.535g (56.9%). M.p. 135°C. Anal. Found: C, 78.47; H, 5.85; N, 7.39. Calc for $C_{38}H_{33}N_3O_3$: C, 78.73; H, 5.74; N, 7.25. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.60 (6H, d, H2',H6'), 7.33 (6H, m, H3',H5'), 7.00 (6H, d, H3,H5), 6.84 (6H, d, H2,H6), 5.04 (6H, s, CH_2), 2.10 (3H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.22, 149.88, 146.31, 142.30, 129.68, 121.48, 113.95, 68.08, 50.64, 30.69. ESI-MS: Found MH^+ = 580.2592; $C_{38}H_{34}N_3O_3$ requires MH^+ = 580.2600.

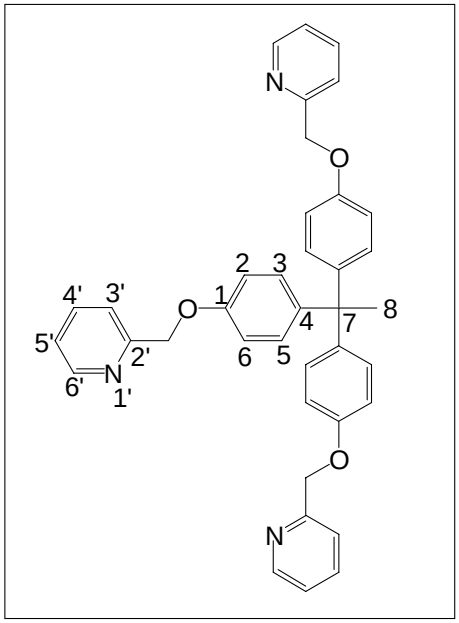
Crystals suitable for X-ray crystallography were obtained by slow evaporation of a methanol/dichloromethane solution of the ligand.

1,1,1-Tris(4-(3-pyridylmethoxy)phenyl)ethane, **4.25**



A mixture of 1,1,1-tris(4-hydroxyphenyl)ethane (1.416g, 4.62mmol) 3-chloromethylpyridine.HCl (2.288g, 13.95mmol) and 40% aqueous tetrabutylammonium hydroxide (7 drops) was refluxed (~80°C) in 25ml of benzene and 7ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **4.25** as a orange oil that solidified on standing. Recrystallisation from ethyl acetate/petroleum ether (1:10) gave **4.25** as an orange solid. Yield 1.761g (65.8%). M.p. 133°C. Anal. Found: C, 78.46; H, 5.78; N, 7.20. Calc for $C_{38}H_{33}N_3O_3$: C, 78.73; H, 5,74; N, 7.25. ^{1}H NMR (300MHz, $CHCl_3$): δ 8.67 (3H, s, H2'), 8.58 (3H, d, H6'), 7.77 (3H, d, H4'), 7.32 (3H, m, H5'), 7.02 (6H, d, H3,H5), 6.87 (6H, d, H2,H6), 5.05 (6H, s, CH_2), 2.11 (3H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.41, 149.32, 148.90, 142.24, 135.30, 132.57, 129.66, 123.48, 113.93, 67.45, 50.64, 30.71. ESI-MS: Found MH^+ = 580.2591; $C_{38}H_{34}N_3O_3$ requires MH^+ = 580.2600.

1,1,1-Tris(4-(2-pyridylmethoxy)phenyl)ethane, **4.26**

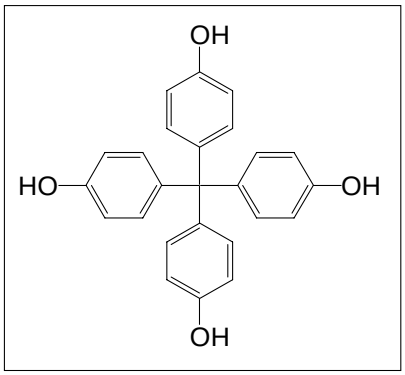


A mixture of 1,1,1-tris(4-hydroxyphenyl)ethane (1.429g, 4.66mmol) 2-chloromethylpyridine.HCl (2.312g, 14.09mmol) and 40% aqueous tetrabutylammonium hydroxide (7 drops) was refluxed (~80°C) in 25ml of benzene and 7ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **4.26** as an orange oil that solidified on standing. Recrystallisation from ethyl acetate/petroleum ether

(1:10) gave **4.26** as a white crystalline solid. Yield 0.346g (12.9%). M.p. 92°C. Anal. Found: C, 78.91; H, 5.73; N, 7.15. Calc for $C_{38}H_{33}N_3O_3$: C, 78.73; H, 5.74; N, 7.25. ^{1}H NMR (300MHz, $CHCl_3$): δ 8.58 (3H, d, H6'), 7.72 (3H, t, H4'), 7.68 (3H, d, H3'), 7.23 (3H, m, H5'), 6.99 (6H, d, H3,H5), 6.89 (6H, d, H2,H6), 5.17 (6H, s, CH_2), 2.10 (3H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 157.29, 156.36, 149.05, 142.07, 136.74, 129.59, 122.49, 121.17, 113.89, 70.49, 50.55, 30.64. ESI-MS: Found MH^+ = 580.2596; $C_{38}H_{34}N_3O_3$ requires MH^+ = 580.2600.

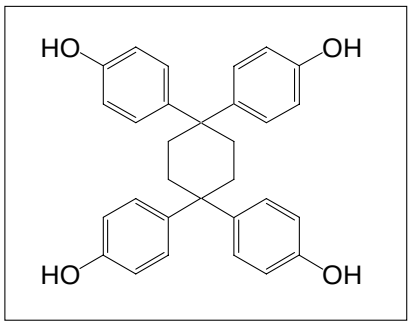
Attempted syntheses of other multi-armed ligand precursors and ligands

Attempted synthesis of tetra(4-hydroxyphenyl)methane, **4.29**



A mixture of 4,4'-dihydroxybenzophenone (3.79g, 17.7mmol) and phenol (6.01g, 63.8mmol) in 1,4-dioxane (10ml) and water (10ml) was stirred at 0°C. At 0°C 20ml of concentrated H_2SO_4 was added dropwise.[176] The mixture initially went a muddy orange/yellow on addition of the concentrated HCl then a yellow colour after the rest of the HCl was added. The mixture was allowed to warm to room temperature and stirred for 4 days. After 4 days the solution was a green colour. The resulting mixture was poured onto 100ml ice-water and extracted with ethyl acetate (3x 80mls). The ethyl acetate layers were combined and washed with water and brine, dried over $MgSO_4$ and reduced *in vacuo* to give pale a orange solid. Analysis of this solid by NMR and TLC showed it to be a mixture of the two starting materials (4,4'-dihydroxybenzophenone and phenol).

Attempted synthesis of 1,1,4,4-tetrakis(4-hydroxphenyl)cyclohexane, **4.31**

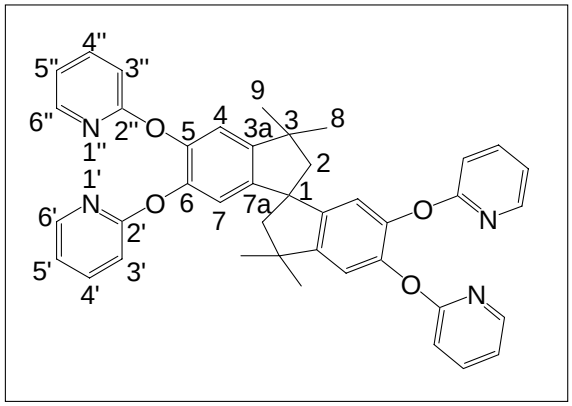


Attempt A: A mixture of 1,4-cyclohexanedione (1.985g, 17.7mmol) and phenol (11.329g, 120.36mmol) in 1,4-dioxane (10ml) and water (10ml) was stirred at 0°C.[176] At 0°C 20ml of concentrated H_2SO_4 was added dropwise. The mixture went through a succession of colour changes from orange to green then red. The mixture was then stirred at room temperature for 4 days. After 4 days the solution was a deep purple colour. The resulting mixture was poured onto 100ml ice-water and extracted with ethyl acetate (3x 80mls). The ethyl acetate layers were washed with water and brine, dried over $MgSO_4$ and reduced *in vacuo* to a brown oil that solidified on standing. Subsequent NMR analysis of the brown solid showed it to be saturated in excess phenol with small traces of other products. The brown solid was washed several times with dichloromethane to remove the excess phenol. However, despite numerous attempts the desired tetraphenol product was unable to be isolated or identified.

Attempt B: This melt synthesis was adapted from a US Patent.[247] A mixture of 1,4-cyclohexanedione (2.00g, 17.8mmol) and phenol (26.85g, 285mmol) was heated to melt at 50°C forming a red solution. Concentrated HCl (1ml) was added to the solution and the solution immediately went green then brown. The reaction was continuously monitored for the next few hours and then stirred at 50°C overnight. TLC showed the presence of two starting materials and a potential product in the mixture. The mixture was heavily contaminated with excess phenol; therefore most of the phenol was distilled off (~10.51g). The remainder of the red mixture was treated with 100ml of toluene, stirred vigorously and filtered. The resulting pink precipitate was rinsed twice with toluene. Analysis showed there to be several different products in the mixture as well as unreacted phenol. Attempts were made to separate and identify some of these products by column chromatography; however no identifiable products came off the column apart from phenol.

Preparation of the 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol based ligands

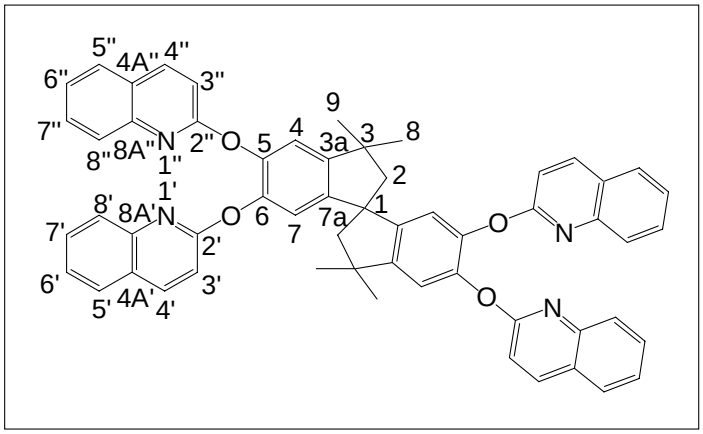
5,5',6,6'-tetra(2-pyridyloxy)-3,3,3'3'-tetramethyl-1,1'-spirobisindane, **4.33**



A mixture of 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol (2.40g, 7.05mmol) and potassium carbonate (4.98g, 36.03mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Bromopyridine (4.58g, 28.99mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (30ml) and H_2O (20ml) and extracted with $CHCl_3$ (4x60mls). Recrystallisation from acetone/water gave **4.33** as a white crystalline solid. Yield 2.12g (46.3%). M.p. 169-171°C. Anal. Found: C, 75.75; H, 5.47; N, 8.63. Calc. for $C_{41}H_{36}N_4O_4$: C, 75.91; H, 5.59; N, 8.64. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.08, 8.00 (4H, d, H6',H6''), 7.53, 7.02 (4H, t, H4',H4''), 7.02 (2H, s, H4), 6.87, 6.83 (4H, t, H5',H5''), 6.81 (2H, s, H7), 6.68, 6.62 (4H, d, H3',H3''), 2.44 (2H, d, H2a), 2.38 (2H, d, H2b), 1.38 (6H, s, H8), 1.37 (6H, s, H9). ^{13}C NMR (75MHz, $CDCl_3$): δ 163.19, 163.13, 149.51, 147.35, 147.31, 147.24, 144.97, 144.64, 138.98, 138.89, 119.09, 118.05, 117.91, 116.49, 110.72, 110.47, 59.39, 57.37, 43.40, 31.54, 30.18. ESI-MS: Found MH^+ = 649.2793; $C_{41}H_{37}N_4O_4$ requires MH^+ = 649.2815.

Colourless crystals suitable for X-ray crystallography were obtained out from the mother liquor of the recrystallisation.

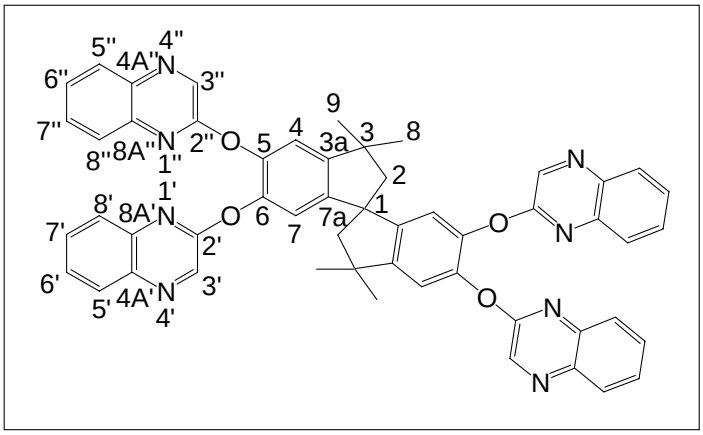
5,5',6,6'-tetra(2-quinolyloxy)-3,3,3'3'-tetramethyl-1,1'-spirobisindane, **4.35**



A mixture of 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol (0.60g, 1.76mmol) and potassium carbonate (2.534g, 18.33mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Chloroquinoline (1.168g, 7.14mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (30ml) and H_2O (20ml) and extracted with $CHCl_3$ (4x50mls). Recrystallisation from acetone/water gave **4.35** as a yellow solid. Yield 0.954g (63.8%). M.p. 196-197°C. Anal. Found: C, 79.82; H, 5.37; N, 6.49. Calc. for $C_{57}H_{44}N_4O_4.½H_2O$: C, 79.79; H, 5.29; N, 6.53. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.12, 8.04 (4H, d, H4',4H"), 7.91, 7.82 (4H, d, H8',H8"), 7.62, 7.54 (4H, d, H5',H5"), 7.47, 7.42 (4H, t, H7',H7"), 7.32, 7.27 (4H, t, H6',H6"), 7.18 (2H, s, H4), 7.05 (2H, s, H7), 6.92, 6.87 (4H, d, H3',H3"), 2.56 (2H, d, H2a), 2.49 (2H, d, H2b), 1.46 (6H, s, H8), 1.44 (6H, s, H9). ^{13}C NMR (75MHz, $CDCl_3$): δ 161.88, 161.18, 149.47, 147.30, 146.11, 146.06, 144.90, 144.58, 139.28, 139.18, 129.36, 127.61, 127.58, 127.06, 127.02, 125.47, 125.41, 124.43, 124.31, 119.54, 116.76, 112.12, 111.88, 59.50, 57.49, 51.08, 43.51, 31.59, 30.26. ESI-MS: Found MH^+ = 849.3450; $C_{57}H_{45}N_4O_4$ requires MH^+ = 849.3441.

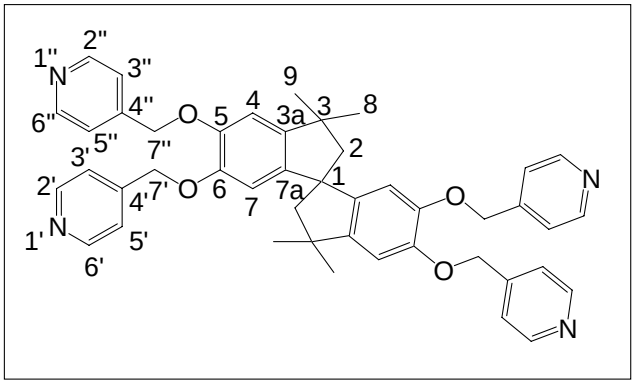
Colourless crystals suitable for X-ray crystallography were grown by slow evaporation of a solution of the ligand and $CoBr_2$ in acetone.

5,5',6,6'-tetra(2-quinoxalinyloxy)-3,3,3'3'-tetramethyl-1,1'-spirobisindane, **4.36**



A mixture of 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol (0.588g, 1.727mmol) and potassium carbonate (2.435g, 17.62mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Chloroquinoline (1.25g, 7.59mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (30ml) and H_2O (20ml) and extracted with $CHCl_3$ (3x80mls). Recrystallisation from acetone/water gave **4.36** as a yellow solid. Yield 0.793g (53.9%). M.p. 244-245°C. Anal. Found: C, 72.84; H, 4.68; N, 12.69. Calc. for $C_{53}H_{40}N_8O_4.H_2O$: C, 73.09; H, 4.86; N, 12.87. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.46, 8.38 (4H, s, H3',H3"), 7.94, 7.86 (4H, d, H8',H8"), 7.52, 7.50 (4H, d, H5',H5"), 7.45, 7.38 (6H, m, H6',H6",H7',H7"), 7.23 (2H, s, H4), 7.13 (2H, s, H7), 2.60 (2H, d, H2a), 2.53 (2H, d, H2b), 1.50 (6H, s, H8), 1.48 (6H, s, H9). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.17, 150.30, 147.87, 143.81, 143.44, 139.71, 139.64, 139.49, 139.42, 138.31, 138.14, 130.15, 130.08, 128.74, 128.63, 127.38, 127.35, 127.20, 119.64, 116.83, 104.68, 59.37, 57.57, 51.10, 43.68, 31.55, 30.19. ESI-MS: Found MH^+ = 853.3275; $C_{53}H_{41}N_8O_4$ requires MH^+ = 853.3251.

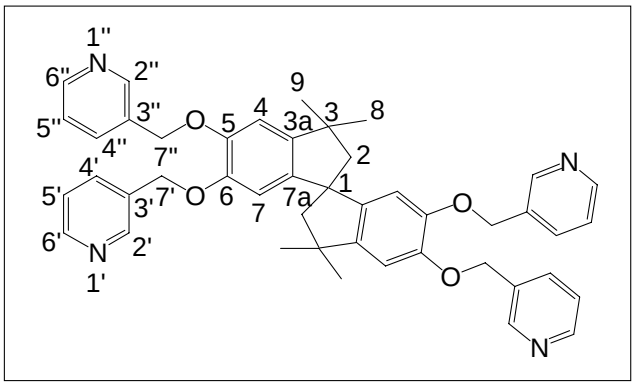
5,5',6,6'-tetra(4-pyridylmethoxy)-3,3,3'3'-tetramethyl-1,1'-spirobisindane, **4.37**



A mixture of 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol (3.16g, 9.3mmol), 4-chloromethylpyridine.HCl (6.18g, 37.67mmol) and 40% aqueous tetrabutylammonium hydroxide (7 drops) was refluxed (~80°C) in 25ml of benzene and 7ml of 40% aqueous

sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **4.37** as a yellow solid. Recrystallisation from ethyl acetate/petroleum ether (1:10) gave **4.37** as a yellow solid. Yield 2.226g (34%). M.p. 98°C. Anal. Found: C, 74.99; H, 6.66; N, 6.47. Calc. for $C_{45}H_{44}N_4O_2.½CH_3CO_2C_2H_5$: C, 75.38; H, 6.46; N, 7.48. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.61, 8.54 (8H, d, H2',H2",H6',H6"), 7.42, 7.32 (8H, d, H3',H3",H5',H5"), 6.75 (2H, s, H4), 6.33 (2H, s, H7), 5.18, 4.97 (8H, s, H7',H7"), 2.30 (2H, d, H2a), 2.04 (2H, d, H2b), 1.31 (6H, s, H8), 1.29 (6H, s, H9). ^{13}C NMR (75MHz, $CDCl_3$): δ 149.66, 149.54, 148.20, 148.03, 146.69, 146.55, 145.66, 143.16, 121.56, 110.39, 108.32, 69.67, 69.56, 59.32, 57.41, 43.24, 31.55, 31.43, 30.32. ESI-MS: Found MH^+ = 705.3471; $C_{45}H_{45}N_4O_4$ requires MH^+ = 705.3441.

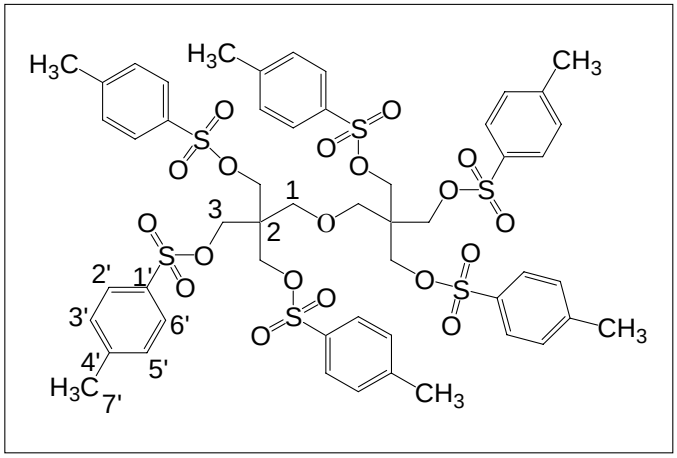
5,5',6,6'-tetra(3-pyridylmethoxy)-3,3,3'3'-tetramethyl-1,1'-spirobisindane, **4.38**



A mixture of 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol (3.11g, 9.14mmol), 3-chloromethylpyridine.HCl (6.187g, 37.72mmol) and 40% aqueous tetrabutylammonium hydroxide (7 drops) was refluxed (~80°C) in 25ml of benzene and 7ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **4.38** as a brown solid. Recrystallisation from ethyl acetate/petroleum ether (1:10) gave **4.38** as a brown solid. Flash chromatography (20g silica, 80:20 ethyl acetate/methanol) and recrystallisation from acetone/water gave **4.38** as a white solid. Yield 2.12g (32.9%). M.p. 104-105°C. Anal. Found: C, 74.44; H, 6.27; N, 7.44. Calc. for $C_{45}H_{44}N_4O_4.H_2O$: C, 74.44; H, 6.41; N, 7.75. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.68, 8.58 (4H, d, H2',H2"), 8.56, 8.50 (4H, d, H6',H6"), 7.80, 7.70 (4H, d, H4',H4"), 6.78 (2H, s, H4), 6.37 (2H, s, H7), 5.15, 4.96 (8H, s, H7',H7"), 2.31 (2H, d, H2a), 2.15 (2H, d, H2b), 1.33 (6H, s, H8), 1.30 (6H, s, H9). ^{13}C NMR (75MHz, $CDCl_3$): δ 149.33, 149.22, 148.93, 148.46, 148.31, 145.63, 143.28, 135.34, 135.33, 132.81, 132.68, 123.47, 123.35, 110.88, 108.78, 69.27, 69.15, 59.37, 57.40, 43.25, 31.50, 30.35. ESI-MS: Found MH^+ = 705.3446; $C_{45}H_{45}N_4O_4$ requires MH^+ = 705.3441.

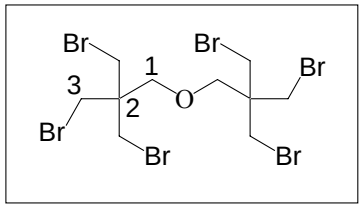
Preparation of the dipentaerythritol based ligands

Preparation of dipentaerythritolhexatosylate, **4.51**



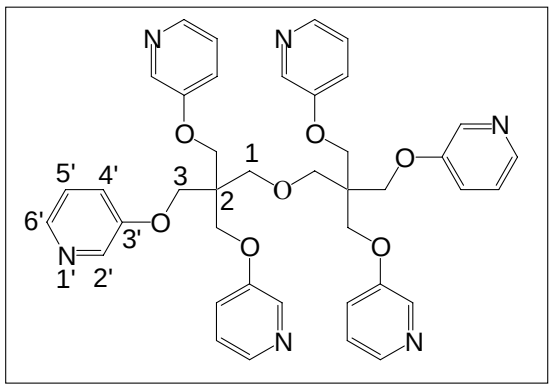
Dipentaerythritol (3.52g, 13.8mmol) was stirred in 10ml of pyridine. A solution of TsCl (18.47g, 96.8mmol) in 25ml of pyridine was added dropwise through a funnel. After the addition was complete, the yellow solution was stirred for 48 hours at room temperature. The mixture was poured onto 50ml of ice-water and the resulting precipitate was filtered and dried under reduced pressure at 50°C over night. Recrystallisation from acetone gave **4.51** as a white solid.[260] Yield 15.33g (95%). M.p.120-121°C. Anal. Found: C, 53.23; H, 5.02. Calc. for $C_{52}H_{58}O_{19}S_6$: C, 52.96; H, 4.96. ^{1}H NMR (300MHz, $CHCl_3$): δ 7.70 (12H, d, H2',H6'), 7.36 (12H, d, H3',H6'), 3.81 (12H, s, H3), 3.17 (4H, s, H1), 2.16 (18H, s, H7'). ^{13}C NMR (75MHz, $CDCl_3$): δ 145.46, 131.74, 130.13, 127.94, 67.87, 66.60, 43.71, 21.67.

Preparation of dipentaerythritolhexabromide, **4.52**



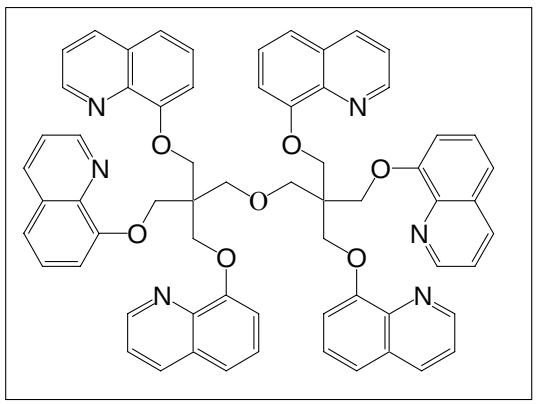
Dipentaerythritolhexatosylate (6.48g, 5.5mmol) was dissolved in 40ml dimethylacetamide. Sodium bromide (8.51g, 8.3mmol) was added and the resulting suspension was heated at 150°C for 2 hours. The mixture was poured onto ice-water and the precipitate was filtered and dried under reduced pressure overnight. Recrystallisation from 3:1 dichloromethane/methanol gave **4.52** as a pale brown solid.[260] Yield 2.73g (53%). M.p.101-102°C. Anal. Found: C, 18.94; H, 2.56. Calc. for $C_{10}H_{16}Br_6O$: C, 19.01; H, 2.55. ^{1}H NMR (300MHz, $CHCl_3$): δ 3.58 (12H, s, H3), 3.53 (4H, s, H1). ^{13}C NMR (75MHz, $CDCl_3$): δ 70.56, 43.73, 34.48.

Preparation of dipentaerythritol hexa(3-pyridyl)ether, **4.54**



3-Hydroxypyridine (1.19g, 12.5mmol) was dissolved in 40ml of dry DMSO and then cooled over ice under argon. Potassium tert-butoxide (1.41g, 12.5mmol) was quickly added and the mixture was allowed to warm to room temperature while stirring for 10 minutes. Dipentaerythritolhexabromide (1.07g, 1.14mmol) was then added and the mixture was refluxed at 120°C for 4 days. The resulting mixture was poured onto 150ml ice-water, neutralized with a few drops of concentrated NaOH solution, extracted with $CHCl_3$ (3x100mls) and washed with water and brine. The solvent was then removed *in vacuo* to give **4.54** as a pale brown solid. Recrystallisation from 1:1 petroleum ether/ethyl acetate gave **4.54** as a sandy coloured solid.[264] Yield 0.509g (5.6%). M.p. 150-153°C. Anal. Found: C, 65.73; H, 5.82; N, 10.78. Calc. for $C_{40}H_{40}N_6O_7.CH_3CO_2C_2H_5$: C, 65.86; H, 6.01; N, 10.44. ^{1}H NMR (300MHz, $CHCl_3$): δ 8.25 (6H, d, H2'), 8.21 (6H, d, H6'), 7.15 (6H, m, H5'), 7.07 (6H, m, H4'), 4.18 (12H, s, H3), 3.87 (4H, s, H1). ^{13}C NMR (75MHz, $CDCl_3$): δ 154.57, 142.56, 137.79, 123.83, 120.80, 69.45, 66.42, 45.08. ESI-MS: Found MH^+ = 717.3009; $C_{40}H_{41}N_6O_7$ requires MH^+ = 717.3037.

Attempted synthesis of dipentaerythritol hexa(8-quinolyloxy)ether, **4.53**

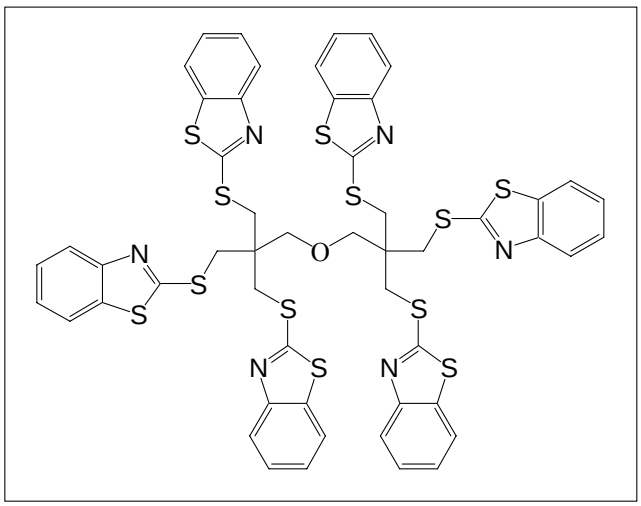


Attempt A: Dipentaerythritolhexabromide (0.500g, 0.532mmol) dissolved in 10ml dry DMF was added dropwise to a stirred solution of 8-hydroxyquinoline (0.309g, 2.12mmol) and KOH (0.119g, 2.12mmol) in 10ml of DMF at 90°C.[192, 255, 261-263] The mixture was kept at 90°C for 24 hours. The solution was cooled and a brown precipitate was filtered off. The precipitate was identified as KBr. The filtrate was poured onto 100ml of water, extracted with $CHCl_3$ (3x100mls) and dried with Na_2SO_4 and concentrated *in vacuo* to a brown

residue. Analysis showed there to be none of the desired product in the residue. It was thought that the product might still be in the aqueous layer. Therefore, saturated aqueous $NaHCO_3$ was added dropwise to the aqueous layer to make it more basic and then it was extracted with dichloromethane (3x100mls), dried with Na_2SO_4 and concentrated down *in vacuo* to a red/brown solid (0.453g). Subsequent analysis was unable to identify or isolate the desired product.

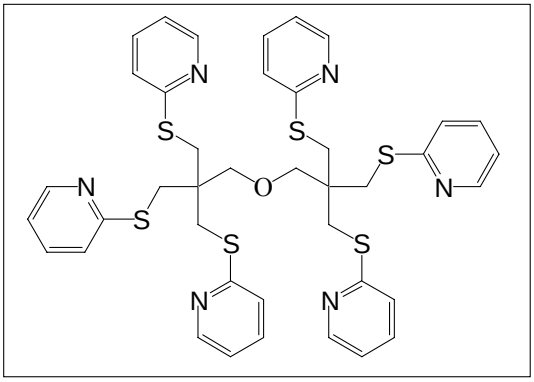
Attempt B: 8-Hydroxyquinoline (2.049g, 1.41mmol) was dissolved in 40ml of dry DMSO and then cooled over ice under argon. Potassium tert-butoxide (1.58g, 1.41mmol) was quickly added and the mixture was allowed to warm to room temperature whilst stirring for 10 minutes. Dipentaerythritolhexabromide (1.51g, 1.28mmol) was then added and the mixture was heated to 130°C for 2 days.[264] The resulting mixture was poured onto 150ml ice-water, neutralized with a couple of drops of concentrated NaOH solution and extracted with chloroform (3x100mls). The chloroform extracts were washed with water and brine, dried with $NaCO_3$ and concentrated *in vacuo* to give a dark brown crystalline solid (1.83g). Subsequent analysis of the solid was unable to identify or isolate the desired product.

Attempted synthesis of dipentaerythritol hexa(benzothiazol-2-yl)sulfide, **4.55**



Dipentaerythritolhexabromide (0.505g, 0.537mmol) dissolved in 10ml dry DMF was added drop-wise to a stirred solution of 2-mercaptobenzothiazole (0.539g, 3.22mmol) and KOH (0.181g, 3.22mmol) in 10ml of DMF at 90°C.[192, 255, 261-263] The mixture was kept at 90°C for 24 hours. A 1ml sample was taken after 24 hours, indicating that it had not reacted. The reaction was left heating for a further 2 days and analysis by NMR and TLC showed that it had not reacted.

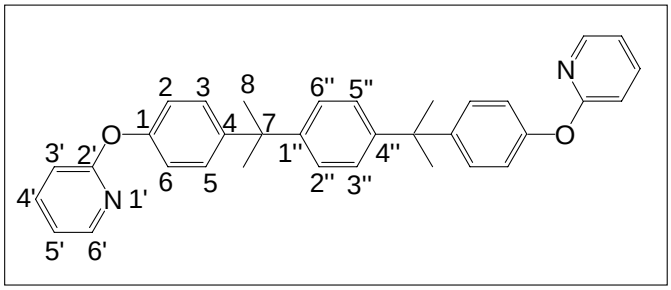
Attempted synthesis of dipentaerythritol hexa(2-pyridyl)sulfide, **4.56**



Dipentaerythritolhexabromide (0.501g, 0.533mmol) dissolved in 10ml dry DMF was added dropwise to a stirred solution of 2-mercaptopyridine (0.356g, 3.19mmol) and KOH (0.179g, 3.19mmol) in 10ml of DMF at 90°C.[192, 255, 261-263] The mixture was kept at 90°C for 8 hours. A 1ml sample was taken after 24 hours, indicating that it had not reacted. The reaction was left heating at 90°C for another week. After 1 week the mixture was cooled down and filtered. The filtrate was concentrated *in vacuo* to a brown residue. The residue was dissolved in 10ml dichloromethane, washed twice with dilute NaOH solution (~40ml) and 40ml of water. The dichloromethane layer was extracted, dried with Na_2SO_4 and concentrated *in vacuo* to give a brown oil. Subsequent analysis of the solid was unable to identify or isolate any product.

Preparation of the Bisphenol P based ligands

1,4-Di(2-(4-(2-pyridyloxy)phenyl)prop-2-yl)benzene, **5.10**

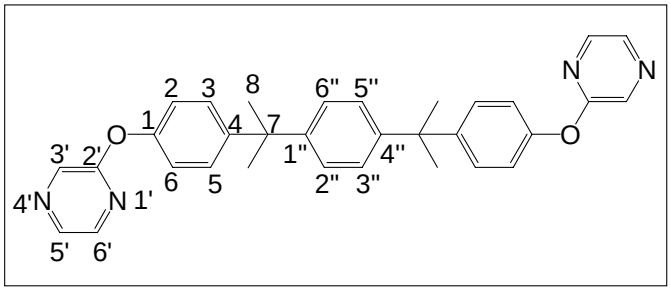


A mixture of Bisphenol P (2.442g, 7.05mmol) and potassium carbonate (4.23g, 30.61mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Bromopyridine (2.31g, 14.62mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (4x60mls). Recrystallisation from acetone/water gave **5.10** as a pale yellow solid. Yield 3.53g (100%). M.p. 137-138°C. Anal. Found: C, 81.32; H, 6.67; N, 5.44. Calc. for $C_{34}H_{32}N_2O_2$: C, 81.57; H, 6.44; N, 5.60. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.20 (2H, d, H6'), 7.66 (2H, t, H4'), 7.26 (4H, d, H3,H5), 7.15 (4H, s, H2'',H3'',H5'',H6''), 7.02 (4H, d, H2,H6), 6.98 (2H, t, H5'), 6.87 (2H, d, H3'), 1.67 (12H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 163.68, 151.82, 147.60,

147.60, 146.91, 139.50, 128.09, 126.32, 120.25, 118.34, 111.48, 42.17, 30.84. ESI-MS: Found MH^+ = 501.2553; $C_{34}H_{33}N_2O_2$ requires MH^+ = 501.2542.

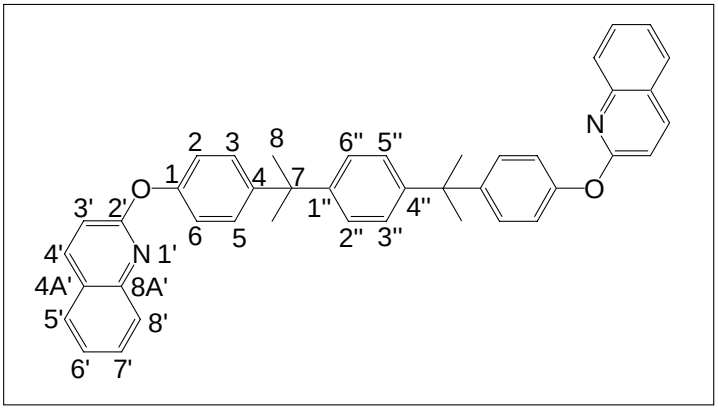
Colourless crystals suitable for X-ray crystallography were grown from a solution of the ligand in dichloromethane and $ZnBr_2$ in methanol.

1,4-Di(2-(4-(2-pyrazinyloxy)phenyl)prop-2-yl)benzene, **5.11**



A mixture of Bisphenol P (1.198g, 3.46mmol) and potassium carbonate (1.99g, 14.4mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. Chloropyrazine (0.812g, 7.09mmol) was then quickly added to this solution and the mixture was heated to reflux (~130°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x50mls). Recrystallisation from acetone/water gave **5.11** as a white crystalline solid. Yield 1.639g (69%). M.p. 133.5-135°C. Anal. Found: C, 76.20; H, 6.09; N, 11.08. Calc. for $C_{32}H_{30}N_4O_2$: C, 76.47; H, 6.02; N, 11.15. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.39 (2H, s, H3'), 8.25 (2H, s, H6'), 8.12 (2H, s, H5'), 7.29 (4H, d, H3,H5), 7.15 (4H, s, H2",H3",H5",H6"), 7.06 (4H, d, H2,H6), 1.68 (12H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 160.14, 150.70, 147.66, 147.44, 141.06, 138.28, 135.80, 128.15, 126.30, 120.30, 42.20, 30.77. ESI-MS: Found MH^+ = 503.2423; $C_{32}H_{31}N_4O_2$ requires MH^+ = 503.2447.

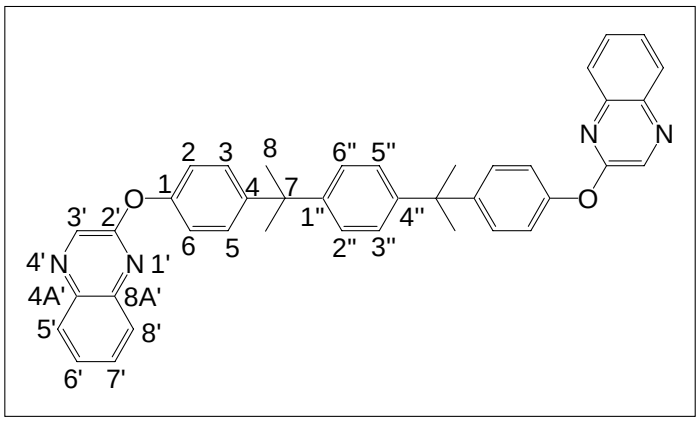
1,4-Di(2-(4-(2-quinolyloxy)phenyl)prop-2-yl)benzene, **5.12**



A mixture of Bisphenol P (1.225g, 3.53mmol) and potassium carbonate (1.962g, 14.2mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Chloroquinoline (1.167g, 7.13mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x50mls). Recrystallisation from acetone/water gave **5.12** as a white solid. Yield 1.833g (86.6%). M.p. 210-211°C. Anal. Found: C, 83.69; H, 5.91; N, 4.61. Calc. for $C_{42}H_{36}N_2O_2$: C, 83.97; H, 6.04; N, 4.66. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.10 (2H, d, H4'), 7.82 (2H, d, H8'), 7.74 (2H, d, H5'), 7.61 (2H, t, H7'), 7.40 (2H, t, H6'), 7.29 (4H, d, H3,H5), 7.19 (4H, s, H2'',H3'',H5'',H6''), 7.16 (4H, d, H2,H6), 7.04 (2H, d, H3'), 1.71 (12H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 161.65, 151.57, 147.65, 147.02, 146.39, 139.76, 129.77, 127.97, 127.84, 127.31, 126.37, 125.61, 124.79, 120.48, 112.61, 42.26, 30.92. ESI-MS: Found MH^+ = 601.2825; $C_{42}H_{37}N_2O_2$ requires MH^+ = 601.2855.

Colourless crystals suitable for X-ray crystallography were grown from a solution of the ligand in dichloromethane and $Cu(NO_3)_2$ in methanol.

1,4-Di(2-(4-(2-quinoxalinyloxy)phenyl)prop-2-yl)benzene, **5.13**

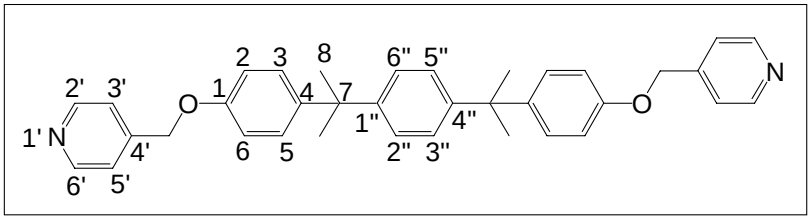


A mixture of Bisphenol P (1.048g, 3.02mmol) and potassium carbonate (1.706g, 12.3mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Chloroquinoxaline

(1.00g, 6.07mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x100mls). Recrystallisation from acetone/water gave **5.13** as a yellow solid. Yield 0.717g (39.4%). M.p. 174-175°C. Anal. Found: C, 78.51; H, 5.82; N, 8.54. Calc. for $C_{40}H_{34}N_4O_2.CH_3COCH_3$: C, 78.16; H, 6.10; N, 8.48. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.67 (2H, s, H3'), 8.07 (2H, d, H8'), 7.79 (2H, d, H5'), 7.66 (2H, t, H6'), 7.62 (2H, t, H7'), 7.32 (4H, d, H3,H5), 7.20 (4H, s, H2",H3",H5",H6"), 7.18 (2H, d, H2,H6), 1.72 (12H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 150.54, 147.79, 147.60, 140.09, 139.34, 139.05, 130.40, 128.76, 128.07, 127.76, 127.46, 126.40, 120.48, 104.70, 42.34, 30.77. ESI-MS: Found MH^+ = 603.2753; $C_{40}H_{35}N_4O_2$ requires MH^+ = 603.2760.

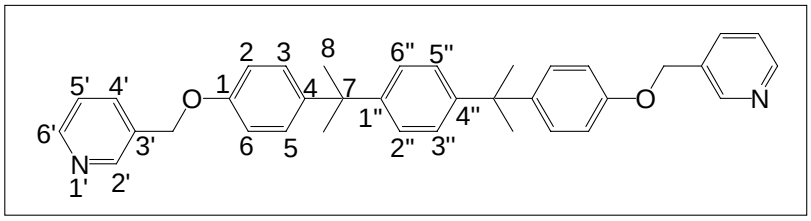
1,4-Di(2-(4-(4-pyridylmethoxy)phenyl)prop-2-yl)benzene, **5.17**

A mixture of Bisphenol P (1.534g, 4.43mmol) 4-chloromethylpyridine.HCl (1.681g, 10.25mmol) and 40% aqueous tetrabutylammonium hydroxide (7 drops) was refluxed (~80°C) in 25ml of benzene and 7ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **5.17** as a orange oil that solidified on standing. Recrystallisation from ethyl acetate/petroleum ether (1:10) gave **5.17** as a cream solid. Yield 1.59g (67.8%). M.p. 76-77°C. Anal. Found: C, 81.65; H, 6.70; N, 5.29. Calc. for $C_{36}H_{36}N_2O_2$: C, 81.79; H, 6.86; N, 5.30. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.61 (4H, d, H2'H6'), 7.35 (4H, d, H3',H5'), 7.15 (4H, d, H3,H5), 7.09 (4H, s, H2",H3",H5",H6"), 6.84 (4H, d, H2,H6), 5.05 (4H, s, CH_2), 1.63 (12H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 155.98, 149.81, 147.73, 146.57, 143.78, 127.91, 126.19, 121.51, 114.06, 68.11, 41.88, 30.83. ESI-MS: Found MH^+ = 529.2846; $C_{36}H_{37}N_2O_2$ requires MH^+ = 529.2855.



Colourless crystals suitable for X-ray crystallography were obtained by slow evaporation of the mother liquor from the recrystallisation.

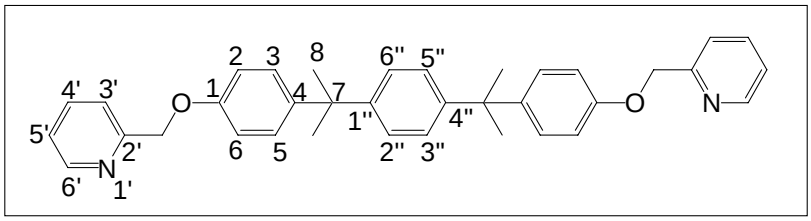
1,4-Di(2-(4-(3-pyridylmethoxy)phenyl)prop-2-yl)benzene, **5.18**



A mixture of Bisphenol P (1.612g, 4.65mmol) 3-chloromethylpyridine.HCl (1.546g, 9.4mmol) and 40% aqueous tetrabutylammonium hydroxide (7 drops) was refluxed (~80°C) in 25ml of benzene and 7ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **5.18** as a orange oil that solidified on standing. Recrystallisation from ethyl acetate/petroleum ether (1:10) gave **5.18** as a white crystalline solid. Yield 2.016g (82.0%). M.p. 176-177°C. Anal. Found: C, 81.93; H, 6.87; N, 5.36. Calc. for $C_{36}H_{36}N_2O_2$: C, 81.79; H, 6.86; N, 5.30. ^{1}H NMR(500MHz, $CHCl_3$): δ 8.67 (2H, d, H2'), 8.57 (2H, d, H6'), 7.76 (2H, d, H4'), 7.31 (2H, m, H5'), 7.16 (4H, d, H3,H5), 7.09 (4H, s, H2'',H3'',H5'',H6''), 6.86 (4H, d, H2,H6), 5.04 (4H, s, CH_2), 1.63 (12H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.19, 149.24, 148.85, 147.74, 143.67, 135.35, 132.75, 127.88, 126.19, 123.51, 114.05, 67.45, 41.87, 30.84. ESI-MS: Found MH^+ = 529.2846; $C_{36}H_{37}N_2O_2$ requires MH^+ = 529.2855.

Colourless crystals suitable for X-ray crystallography were obtained by slow evaporation of the mother liquor from the recrystallisation.

1,4-Di(2-(4-(2-pyridylmethoxy)phenyl)prop-2-yl)benzene, **5.19**



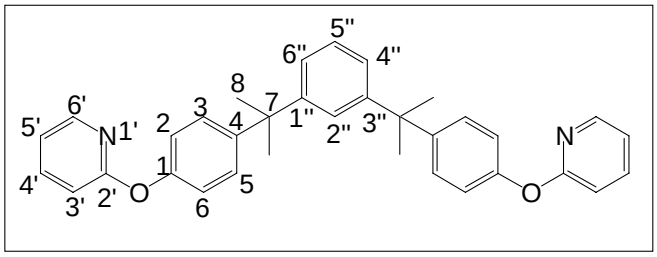
A mixture of Bisphenol P (1.601g, 4.62mmol) 2-chloromethylpyridine.HCl (1.530g, 9.3mmol) and 40% aqueous tetrabutylammonium hydroxide (7 drops) was refluxed (~80°C) in 25ml of benzene and 7ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **5.19** as a white solid. Recrystallisation from ethyl acetate/petroleum ether (1:10) gave **5.19** as a white crystalline solid. Yield 1.951g (79.9%). M.p. 171°C. Anal. Found: C, 81.73; H, 7.03; N, 5.28. Calc. for

$C_{36}H_{36}N_2O_2$: C, 81.79; H, 6.86; N, 5.30. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.58 (2H, d, H6'), 7.72 (2H, t, H4'), 7.69 (2H, d, H3'), 7.54 (2H, m, H5'), 7.15 (4H, d, H3,H5), 7.09 (4H, s, H2",H3",H5",H6"), 6.88 (4H, d, H2,H6), 5.18 (4H, s, CH_2), 1.63 (12H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 157.45, 156.18, 149.02, 147.73, 143.41, 136.85, 127.82, 126.17, 122.52, 121.23, 114.07, 70.49, 41.83, 30.84. ESI-MS: Found MH^+ = 529.2855; $C_{36}H_{37}N_2O_2$ requires MH^+ = 529.2855.

Colourless crystals suitable for X-ray crystallography were grown from a solution of the ligand and $Cu(NO_3)_2$ in a methanol/dichloromethane solution.

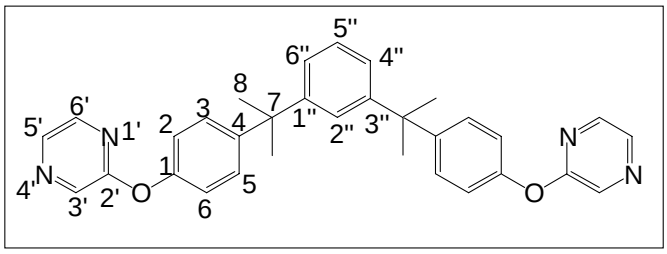
Preparation of the Bisphenol M based ligands

1,3-Di(2-(4-(2-pyridyloxy)phenyl)prop-2-yl)benzene, **5.22**



A mixture of Bisphenol M (2.44g, 7.04mmol) and potassium carbonate (3.96g, 28.65mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Bromopyridine (2.34g, 14.8mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (4x60mls). Recrystallisation from acetone/water gave **5.22** as a white solid. Yield 0.802g (22.7%). M.p. 64-65°C. Anal. Found: C, 80.61; H, 6.92; N, 5.00. Calc. for $C_{34}H_{32}N_2O_2.½CH_3COCH_3$: C, 80.50; H, 6.66; N, 5.29. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.28 (2H, d, H6'), 7.76 (2H, t, H4'), 7.11 (12H, m, H2,H3,H5,H6,H2",H4",H5",H6"), 6.91 (2H, t, H5'), 6.69 (2H, t, H3'), 1.61 (12H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 163.34, 153.94, 149.92, 147.18, 146.99, 140.18, 128.10, 127.68, 127.28, 123.48, 123.27, 119.50, 114.76, 42.60, 30.75. ESI-MS: Found MH^+ = 501.2542; $C_{34}H_{33}N_2O_2$ requires MH^+ = 501.2542.

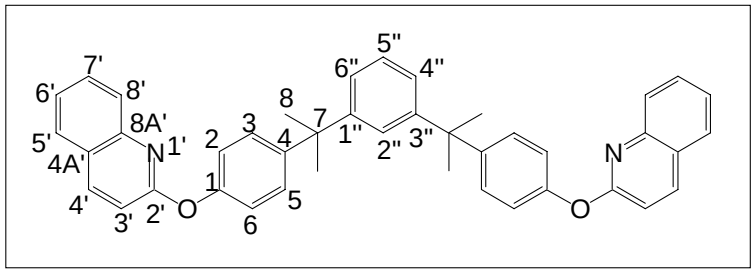
1,3-Di(2-(4-(2-pyrazinyloxy)phenyl)prop-2-yl)benzene, **5.23**



A mixture of Bisphenol M (1.221g, 3.52mmol) and potassium carbonate (1.968g, 14.24mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. Chloropyrazine (0.812g, 7.09mmol) was then quickly added to this solution and the mixture was heated to reflux (~130°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x50mls). Recrystallisation from acetone/water gave **5.23** as a white crystalline solid. Yield 1.665g (94.2%). M.p. 103-104°C. Anal. Found: C, 76.51; H, 6.09; N, 11.05. Calc. for $C_{32}H_{30}N_4O_2$: C, 76.47; H, 6.02; N, 11.15. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.37 (2H, s, H3'), 8.24 (2H, d, H6'), 8.11 (2H, d, H5'), 7.24 (4H, d, H3,H5), 7.19 (1H, t, H5"), 7.14 (1H, s, H2"), 7.09 (2H, d, H4",H6"), 7.03 (4H, d, H2,H6), 1.66 (12H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 160.13, 150.66, 149.82, 147.69, 141.05, 138.26, 135.71, 128.09, 127.58, 125.31, 124.15, 120.28, 42.72, 30.74. ESI-MS: Found MH^+ = 503.2444; $C_{32}H_{31}N_4O_2$ requires MH^+ = 503.2447.

Colourless crystals suitable for X-ray crystallography were grown from a solution of the ligand in dichloromethane and $ZnBr_2$ in methanol.

1,3-Di(2-(4-(2-quinolyloxy)phenyl)prop-2-yl)benzene, **5.24**

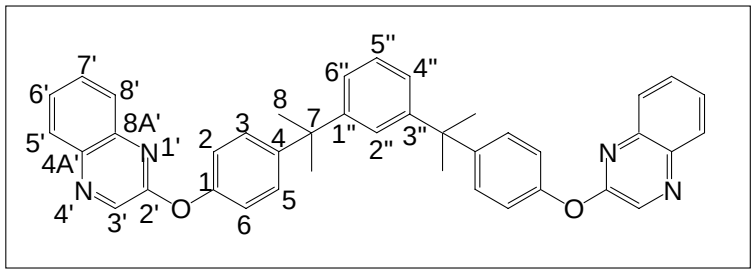


A mixture of Bisphenol M (1.256g, 3.61mmol) and potassium carbonate (1.982g, 14.3mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Chloroquinoline (1.164g, 7.11mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x50mls). Recrystallisation from

acetone/water gave **5.24** as a yellow crystalline solid. Yield 1.742g (80.3%). M.p. 134.5-135.5°C. Anal. Found: C, 83.68; H, 6.12; N, 4.58. Calc. for $C_{42}H_{36}N_2O_2$: C, 83.97; H, 6.04; N, 4.66. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.04 (2H, d, H4'), 7.79 (2H, d, H8'), 7.70 (2H, d, H5'), 7.58 (2H, t, H7'), 7.38 (2H, t, H6'), 7.25 (4H, d, H3,H5), 7.20 (1H, t, H5"), 7.14 (1H, s, H2"), 7.12 (6H, m, H2,H6,H4",H6"), 1.69 (12H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 161.61, 151.51, 150.05, 146.98, 146.36, 139.64, 129.69, 127.87, 127.79, 127.55, 127.26, 125.55, 125.44, 124.70, 124.14, 120.48, 112.51, 42.74, 30.85. ESI-MS: Found MH^+ = 601.2849; $C_{42}H_{37}N_2O_2$ requires MH^+ = 601.2855.

Crystals suitable for X-ray crystallography were obtained by slow evaporation of the mother liquor from the recrystallisation.

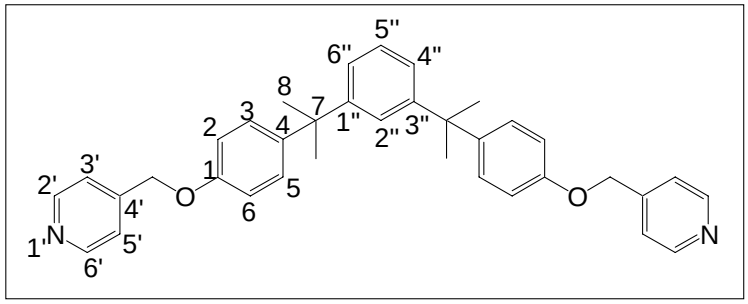
1,3-Di(2-(4-(2-quinoxalinyloxy)phenyl)prop-2-yl)benzene, **5.25**



A mixture of Bisphenol M (1.049g, 3.03mmol) and potassium carbonate (1.703g, 12.3mmol) was stirred in a solution of sulpholane/toluene (10ml/5ml) at room temperature under argon for 45 minutes. 2-Chloroquinoxaline (1.00g, 6.07mmol) was then quickly added to this solution and the mixture was heated to reflux (~180°C) under argon for 48 hours. The resulting mixture was poured onto 10% NaOH soln. (20ml) and H_2O (10ml) and extracted with $CHCl_3$ (3x50mls). Recrystallisation from acetone/water gave **5.25** as an orange solid. Yield 1.42g (77.8%). M.p. 143-144°C. Anal. Found: C, 79.68; H, 5.81; N, 9.05. Calc. for $C_{40}H_{34}N_4O_2$: C, 79.71; H, 5.69; N, 9.30. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.61 (2H, d, H3'), 8.02 (2H, d, H8'), 7.73 (2H, d, H5'), 7.62 (2H, t, H6'), 7.57 (2H, t, H7'), 7.29 (4H, d, H3,H5), 7.25 (1H, t, H5"), 7.18 (1H, s, H2"), 716 (2H, d, H4",H6"), 7.14 (4H, d, H2,H6), 1.71 (12H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.83, 150.47, 149.98, 147.72, 141.98, 139.92, 139.47, 139.16, 130.26, 128.84, 127.96, 127.63, 127.31, 125.60, 124.13, 120.47, 42.81, 30.82. ESI-MS: Found M^+ = 602.2681; $C_{40}H_{34}N_4O_2$ requires M^+ = 602.2682.

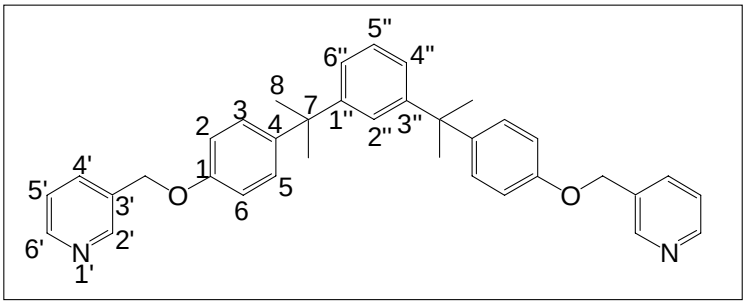
Colourless crystals suitable for X-ray crystallography were grown from a solution of the ligand in acetone and $CoCl_2$ in acetone.

1,3-Di(2-(4-(4-pyridylmethoxy)phenyl)prop-2-yl)benzene, **5.38**



A mixture of Bisphenol M (1.601g, 4.62mmol) 4-chloromethylpyridine.HCl (1.592g, 9.7mmol) and 40% aqueous tetrabutylammonium hydroxide (7 drops) was refluxed (~80°C) in 25ml of benzene and 7ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **5.38** as a orange oil that solidified on standing to give a brown solid. Recrystallisation from ethyl acetate/ petroleum ether (1:10) gave **5.38** as a light brown solid. Yield 2.38g (97.5%). M.p. 91-92°C. Anal. Found: C, 80.45; H, 7.56; N, 5.18. Calc. for $C_{36}H_{36}N_2O_2.½CH_3CO_2C_2H_5$: C, 80.82; H, 7.14; N, 7.08. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.59 (4H, d, H2'H6'), 7.33 (4H, d, H3',H5'), 7.14 (1H, t, H5"), 7.11 (5H, m, H3,H5,H2"), 7.02 (2H, d, H4",H6"), 6.82 (4H, d, H2,H6), 5.05 (4H, s, CH_2), 1.60 (12H, s, H8).^{13}C NMR (75MHz, $CDCl_3$): δ 155.81, 150.03, 149.74, 146.34, 143.71, 127.75, 127.34, 125.12, 123.91, 121.37, 113.92, 67.96, 42.29, 30.75. ESI-MS: Found MH^+ = 529.2870; $C_{36}H_{37}N_2O_2$ requires MH^+ = 529.2855.

1,3-Di(2-(4-(3-pyridylmethoxy)phenyl)prop-2-yl)benzene, **5.39**

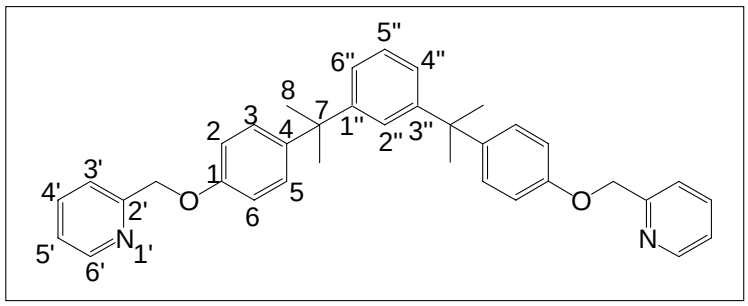


A mixture of Bisphenol M (1.619g, 4.67mmol) 3-chloromethylpyridine.HCl (1.533g, 9.3mmol) and 40% aqueous tetrabutylammonium hydroxide (7 drops) was

refluxed (~80°C) in 25ml of benzene and 7ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **5.39** as a orange oil that solidified on standing to give a brown solid. Yield 2.23g (90.4%). M.p. 72-73°C. Anal. Found: C, 81.49; H, 7.07; N, 5.32. Calc. for $C_{36}H_{36}N_2O_2$: C, 81.79; H, 6.86; N, 5.30. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.65 (2H, d, H2'), 8.55 (2H, d, H6'), 7.74 (2H, d, H4'), 7.27 (2H, t, H5'), 7.12 (4H, d, H3,H5), 7.14 (1H, t, H5"), 7.12 (4H, d, H3,H5), 7.10 (1H, s, H2"), 7.02 (2H, d, H4",H6"), 6.84 (4H, d, H2,H6), 5.02 (4H, s, CH_2), 1.61 (12H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 156.03, 150.06, 149.19, 148.82, 143.60, 135.14, 132.56, 127.73, 127.33, 125.12, 123.92, 123.35, 113.94, 67.36, 42.30, 30.77. ESI-MS: Found MH^+ = 529.2828; $C_{36}H_{37}N_2O_2$ requires MH^+ = 529.2855.

1,3-Di(2-(4-(2-pyridylmethoxy)phenyl)prop-2-yl)benzene, **5.40**

A mixture of Bisphenol M (1.628g, 4.70mmol) 2-chloromethylpyridine.HCl (1.601g, 9.76mmol) and 40% aqueous tetrabutylammonium hydroxide (7 drops) was



refluxed (~80°C) in 25ml of benzene and 7ml of 40% aqueous sodium hydroxide for 2 days. The organic layer was then separated, dried over Na_2SO_4 and concentrated *in vacuo* to give **5.40** as a white solid. Recrystallisation from ethyl acetate/ petroleum ether (1:10) gave **5.40** as a white crystalline solid. Yield 2.076g (83.6%). M.p. 81-82°C. Anal. Found: C, 80.64; H, 7.21; N, 5.28. Calc. for $C_{36}H_{36}N_2O_2.½H_2O$: C, 80.42; H, 6.94; N, 5.21. ^{1}H NMR (500MHz, $CHCl_3$): δ 8.56 (2H, d, H6'), 7.66 (2H, t, H4'), 7.51 (2H, d, H3'), 7.18 (2H, t, H5'), 7.17 (1H, t, H5"), 7.10 (4H, d, H3,H5), 7.08 (1H, s, H2"), 7.01 (2H, d, H4",H6"), 6.86 (4H, d, H2,H6), 5.17 (4H, s, CH_2), 1.60 (12H, s, H8). ^{13}C NMR (75MHz, $CDCl_3$): δ 157.39, 156.08, 150.14, 149.03, 143.41, 136.71, 127.73, 127.33, 125.14, 123.97, 122.45, 121.17, 114.00, 70.48, 42.32, 30.81. ESI-MS: Found MH^+ = 529.2876; $C_{36}H_{37}N_2O_2$ requires MH^+=529.2855

Preparation of complexes

Preparation of complexes with the Bisphenol A ligands

Complexes with 2.19

With cobalt(II) bromide, viz **2.35**

A solution of cobalt(II) bromide (26.3mg, 0.12mmol) dissolved in acetone (3ml) was layered upon a solution of ligand **2.19** (23.3mg, 0.060mmol) dissolved in acetone:dichloromethane (3ml). Beautiful blue block-like crystals formed within minutes of standing on the bench, which were suitable for X-ray crystallography and revealed a 1-dimensional coordination polymer. Yield 24.5mg (62.2%). M.p. 299-303°C. Anal. Found: C, 44.75; H, 4.19; N, 3.59. Calc. for $C_{25}H_{22}N_2O_2Br_2Co.CH_2Cl_2.2H_2O.(CH_3)_2CO$: C, 44.64; H, 4.39; N, 3.59.

With cobalt(II) chloride, viz **2.36**

A solution of cobalt(II) chloride (23.7mg, 0.10mmol) dissolved in acetone (3ml) was layered upon a solution of ligand **2.19** (20.5mg, 0.056mmol) dissolved in acetone:dichloromethane (3ml). Beautiful blue crystal plates of **2.36** formed within minutes of standing on the bench, which were suitable for X-ray crystallography and revealed a 1-dimensional helical polymer. Yield 24.1mg (79.9%). M.p. 265-266°C. Anal. Found: C, 42.39; H, 4.19; N, 3.58. Calc. for $C_{25}H_{22}N_2O_2Cl_2Co.3CH_2Cl_2.3H_2O.(CH_3)_2CO$: C, 42.35; H, 4.59; N, 3.19.

With copper(II) chloride, viz **2.37**

A solution of copper(II) chloride (24.5mg, 0.14mmol) dissolved in methanol (10ml) was layered upon a solution of ligand **2.19** (27.5mg, 0.072mmol) dissolved in dichloromethane (10ml). Slow evaporation over a week gave green plate-like crystals suitable for X-ray crystallography. The X-ray analysis revealed a novel 'necklace' type structure, which is a 1-dimensional polymer chain made up of M_2L_2 macrocyclic units joined by Cu_2Cl_4 squares. Yield 37.4mg (86.7%). M.p. 213-215°C. Anal. Found: C, 51.81; H, 4.04; N, 4.75. Calc. for $C_{25}H_{22}N_2O_2Cl_2Cu.CH_2Cl_2$: C, 51.89; H, 4.02; N, 4.65.

With copper nitrate, viz **2.38**

A solution of copper nitrate (29.0mg, 0.12mmol) dissolved in acetone (5ml) was layered upon a solution of ligand **2.19** (21.7mg, 0.057mmol) dissolved in chloroform (5ml). Slow evaporation of the blue solution to dryness produced blue block-like crystals suitable for X-ray crystallography. X-ray analysis revealed a [2 +2] macrocycle. Yield 21.4mg (47%). M.p. 188-191°C. Anal. Found: C, 47.32; H, 4.06; N, 6.47. Calc. for $C_{25}H_{22}N_4O_8Cu$: C, 47.71; H, 4.38; N, 6.96.

With copper nitrate, viz **2.39a**

A solution of copper nitrate (32.0mg, 0.13mmol) dissolved in methanol (7ml) was layered upon a solution of ligand **2.19** (25.3mg, 0.066mmol) dissolved in dichloromethane (7ml). Slow evaporation of the blue solution produced beautiful blue crystalline plates after a couple of weeks. X-ray analysis revealed a copper dinuclear quadruple helicate. Yield 22.3mg (88%). M.p. 205-208°C. Anal. Found: C, 39.07; H, 3.90; N, 9.93. Calc. for $C_{25}H_{22}N_6O_{14}Cu_2$: C, 39.04; H, 3.76; N, 10.12 analysed as a 2:1 complex.

With copper nitrate, viz **2.39b**

Another batch of the copper helicate complex was prepared in order to try to grow single crystals suitable for X-ray. The copper nitrate (28.1mg, 0.116mmol) was dissolved in methanol (5ml) and layered upon ligand **2.19** (22.5mg, 0.059mmol) dissolved in chloroform (5ml). Slow evaporation of the resulting blue solution to dryness gave clusters of plate-like blue crystals suitable for X-ray crystallography. Once again the crystals were extremely air sensitive. X-ray analysis revealed the copper dinuclear quadruple helicate. Yield 16.8mg (47.8%). M.p. 175-180°C. Anal. Found: C, 50.35; H, 4.37; N, 9.26. Calc. for $C_{25}H_{22}N_4O_8Cu.1½H_2O$: C, 50.29; H, 4.22; N, 9.38 analysed as a 1:1 complex.

With silver hexafluorophosphate, viz **2.40**

A solution of ligand **2.19** (24.5mg, 0.064mmol) was dissolved in chloroform (2ml) and layered upon a solution of silver trifluoromethanesulfonate (16.2mg, 0.064mmol) dissolved in acetone (2ml). Slow evaporation and vapour diffusion of ether into the reaction mixture gave colourless block-like crystals of **2.40** that were suitable for X-ray

crystallography. X-ray analysis revealed a [2+2] macrocycle. Yield 39.6mg (89.4%). M.p. 160-161°C. Anal. Found: C, 48.57; H, 4.17; N, 4.02. Calc. for $C_{25}H_{22}N_2O_2PF_6Ag.(CH_3)_2CO$: C, 48.50; H, 4.07; N, 4.04.

With silver trifluoromethanesulfonate, viz **2.41**

A solution of ligand **2.19** (26.3mg, 0.069mmol) was dissolved in chloroform (2ml) and layered upon a solution of silver trifluoromethanesulfonate (20.6mg, 0.080mmol) dissolved in acetone (2ml). Slow evaporation and vapour diffusion of ether into the reaction mixture gave clumps of unstable colourless plate-like crystals of **2.41** that were suitable for X-ray crystallography. Yield 15.6mg (34.5%). M.p. 186-190°C. Anal. Found: C, 47.37; H, 3.47; N, 4.17. Calc. for $C_{26}H_{22}N_2O_5F_3SAg.H_2O$: C, 47.50; H, 3.68; N, 4.26.

With zinc bromide, viz **2.42**

Zinc bromide (29.3mg, 0.13mmol) was dissolved in methanol (10ml) and layered upon a solution of ligand **2.19** (24.9mg, 0.065mmol) dissolved in dichloromethane (10ml). Slow evaporation of the resulting reaction mixture gave colourless plate-like crystals that were suitable for X-ray crystallography and revealed a 1-dimensional helical polymer. Yield 39mg (61.7%). M.p. 242-245°C. Anal. Found: C, 36.58; H, 3.40; N, 3.29. Calc. for $C_{25}H_{22}N_2O_2Br_2Zn.4CH_2Cl_2.CH_3OH$: C, 36.79; H, 3.50; N, 2.86.

With zinc chloride, viz **2.43**

Zinc chloride (18mg, 0.132mmol) was dissolved in methanol (5ml) and layered upon a solution of ligand **2.19** (24.7mg, 0.065mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting reaction mixture gave colourless block-like crystals of **2.43** that were suitable for X-ray crystallography and revealed a 1-dimensional helical polymer. Yield 15.9mg (42.4%). M.p. 251°C. Anal. Found: C, 55.51; H, 4.32; N, 5.13. Calc. for $C_{25}H_{22}N_2O_2Cl_2Zn.2CH_3OH$: C, 55.64; H, 5.19; N, 4.81.

With copper perchlorate

A solution of copper perchlorate (65.9mg, 0.178mmol) dissolved in methanol (5ml) was layered upon a solution of ligand **2.19** (133.0mg, 0.086mmol) dissolved in dichloromethane (5ml). Small blue crystalline plates grew in solution over the weekend. Unfortunately these were too small and brittle for X-ray crystallography. Yield 27.3mg

(13.5%). M.p. 203°C. Anal. Found: C, 52.70; H, 4.48; N, 4.86. Calc. for $C_{100}H_{88}N_8O_{24}Cl_4Cu_2.3CH_2Cl_2.2H_2O$: C, 52.74; H, 4.21; N, 4.78 revealing a complex M_2L_4 complex.

Complexes with 2.21

With copper(II) chloride, viz **2.44**

A solution of copper(II) chloride (21.8mg, 0.13mmol) dissolved in methanol (10ml) was layered upon a solution of ligand **2.21** (24.6mg, 0.064mmol) dissolved in dichloromethane (10ml). Slow evaporation of the resulting pale green solution gave green plate-like crystals of a M_2L_2 complex. Yield 33.8mg (81.3%). M.p. 265-267°C. Anal. Found: C, 43.96; H, 3.87; N, 8.77. Calc. for $C_{23}H_{20}N_4O_2Cl_2Cu.CH_2Cl_2.2⅔H_2O$: C, 44.22; H, 4.23; N, 8.60.

With silver hexafluorophosphate

A solution of ligand **2.21** (22.4mg, 0.06mmol) in chloroform (3ml) was layered upon a solution of silver hexafluorophosphate (15.2mg, 0.06mmol) dissolved in a solution of acetone (2ml). Immediately a white precipitate formed which was collected by filtration and dried *in vacuo*. Yield 32.1mg (81.8%). M.p. 190-195°C. Anal. Found: C, 42.17; H, 3.46; N, 8.27. Calc. for $C_{23}H_{20}N_4O_2PF_6Ag.H_2O$: C, 42.16; H, 3.38; N, 8.55 revealing a 1:1 complex.

With silver perchlorate

A solution of ligand **2.21** (23.4mg, 0.061mmol) in chloroform (3ml) was layered upon a solution of silver perchlorate (12.6mg, 0.061mmol) dissolved in acetone (2ml). Immediately a white precipitate formed which was collected by filtration and dried *in vacuo*. Yield 26.1mg (65%). Anal. Found: C, 42.84; H, 3.43; N, 8.49. Calc. for $C_{23}H_{20}N_4O_6ClAg.½H_2O.½CHCl_3$: C, 42.74; H, 3.28; N, 8.48 revealing a 1:1 complex.

With silver trifluoromethanesulfonate

A solution of ligand **2.21** (25.5mg, 0.066mmol) in hot acetone (3ml) was layered upon a solution of silver trifluoromethanesulfonate (18.2mg, 0.070mmol) also dissolved in acetone (2ml). Immediately a white precipitate formed which was collected by filtration

and dried *in vacuo*. Yield 21.3mg (50.4%). M.p. 220-222°C. Anal. Found: C, 44.70; H, 3.25; N, 8.59. Calc. for $C_{24}H_{20}N_4O_5F_3SAg$: C, 44.94; H, 3.14; N, 8.74 revealing a 1:1 complex.

Complexes with 2.23

With silver hexafluorophosphate

A solution of ligand **2.23** (15.4mg, 0.032mmol) in chloroform (3ml) was layered upon a solution of silver hexafluorophosphate (8.1mg, 0.032mmol) dissolved in acetone (2ml). Slow evaporation of the resulting colourless solution and vapour diffusion of ether into the reaction mixture, gave a colourless crystalline material. A few weeks later this was collected by filtration and dried *in vacuo*. Yield 21.8mg (77%). M.p. 186-188°C. Anal. Found: C, 48.10; H, 3.78; N, 3.14. Calc. for $C_{33}H_{26}N_2O_2PF_6Ag.CHCl_3.½(CH_3)_2CO$: C, 48.24; H, 3.42; N, 3.17 revealing a 1:1 complex.

With silver perchlorate

A solution of ligand **2.23** (9.6mg, 0.020mmol) in chloroform (3ml) was layered upon a solution of silver hexafluorophosphate (7.5mg, 0.036mmol) dissolved in acetone (2ml). Slow evaporation of the resulting colourless solution and vapour diffusion of ether into the reaction mixture, gave a colourless crystalline material. A few weeks later this was collected by filtration and dried *in vacuo*. Yield 5.4mg (37.2%). M.p. 195-200°C. Anal. Found: C, 54.46; H, 4.11; N, 3.80. Calc. for $C_{33}H_{26}N_2O_6ClAg.2H_2O$: C, 54.60; H, 4.17; N, 3.86 revealing a 1:1 complex.

With silver trifluoromethanesulfonate

A solution of ligand **2.23** (18.3mg, 0.038mmol) in 1:1 chloroform:dichloromethane (4ml) was layered upon a solution of silver trifluoromethanesulfonate (9.80mg, 0.038mmol) dissolved in acetone (2ml). Slow evaporation of the resulting colourless solution and vapour diffusion of ether gave a white precipitate on standing. A few weeks later the white precipitate was collected by filtration and dried *in vacuo*. Yield 27.6mg (93%). M.p. 154-156°C. Anal. Found: C, 53.13; H, 3.36; N, 3.51. Calc. for $C_{34}H_{26}N_2O_5F_3SAg.½CH_2Cl_2$: C, 52.99; H, 3.48; N, 3.58 revealing a 1:1 complex.

Complexes with 2.25

With silver hexafluorophosphate

A solution of ligand **2.25** (20.8mg, 0.043mmol) in chloroform (2ml) was layered upon a solution of silver hexafluorophosphate (12.5mg, 0.049mmol) dissolved in a solution of acetone (2ml). A white precipitate formed immediately which was filtered off and dried *in vacuo*. Yield 13.3mg (39%). M.p. 225-228°C. Anal. Found: C, 51.96; H, 3.42; N, 7.69. Calc. for $C_{31}H_{24}N_4O_2PF_6Ag.(CH_3)_2CO$: C, 51.34; H, 3.80; N, 7.04 revealing a 1:1 complex.

With silver perchlorate

A solution of ligand **2.25** (20.7mg, 0.043mmol) in chloroform (2ml) was layered upon a solution of silver perchlorate (10.3mg, 0.049mmol) dissolved in a solution of acetone (2ml). A white precipitate formed immediately which was filtered off and dried *in vacuo*. Yield 20.2mg (29%). M.p. 238-239°C. Anal. Found: C, 45.53; H, 3.09; N, 6.74. Calc. for $C_{62}H_{48}N_8O_{16}Cl_3Ag_3.2H_2O$: C, 45.77; H, 3.22; N, 6.89 revealing a M_3L_2 complex.

With silver trifluoromethanesulfonate

A solution of ligand **2.25** (24.3mg, 0.05mmol) in hot acetone (3ml) was layered upon a solution of silver trifluoromethanesulfonate (12.9mg, 0.05mmol) also dissolved in acetone (2ml). Slow evaporation of the resulting yellow solution gave an off-white precipitate. The white precipitate was recrystallised from acetonitrile to give a crystalline solid. The crystalline solid was collected by filtration and dried *in vacuo*. Yield 35.2mg (89%). M.p. 258-261°C. Anal. Found: C, 51.88; H, 3.55; N, 9.43. Calc. for $C_{32}H_{24}N_4O_2F_3SAg.1¼CH_3CN$: C, 52.27; H, 3.53; N, 9.28 revealing a 1:1 complex.

Complexes with 2.45

With copper(II) chloride

A solution of copper(II) chloride (18.0mg, 0.11mmol) dissolved in methanol (10ml) was layered upon a solution of ligand **2.45** (21.7mg, 0.05mmol) dissolved in dichloromethane (10ml). Immediately a pale green precipitate formed at the boundary

between the two solutions. A few weeks later the pale green precipitate was filtered off. Yield 26.3mg (73%). M.p. 170°C. Anal. Found: C, 44.69; H, 3.91; N, 3.77. Calc. for $C_{27}H_{26}N_2O_2Cl_4Cu_2.2½H_2O$: C, 44.76; H, 4.31; N, 3.87 revealing a M_2L complex.

With copper(I) iodide

Copper(I) iodide (19.3mg, 0.10mmol) and ligand **2.45** (20.4mg, 0.05mmol) were both dissolved in hot acetonitrile (10ml) and combined. Immediately a pale brown precipitate formed which was collected by filtration and dried *in vacuo*. Yield 29.4mg (74.4%). M.p. 174-179°C. Anal. Found: C, 40.60; H, 3.35; N, 3.63. Calc. for $C_{27}H_{26}N_2O_2I_2Cu_2$: C, 40.98; H, 3.31; N, 3.54 revealing a M_2L complex.

With copper nitrate

A solution of copper nitrate (25.6mg, 0.11mmol) dissolved in methanol (10ml) was layered upon a solution of ligand **2.45** (20.7mg, 0.05mmol) dissolved in dichloromethane (10ml). Slow evaporation gave a turquoise blue solid, which was filtered off and dried *in vacuo*. Yield 27mg (61.8%). M.p. 106-109°C. Anal. Found: C, 36.91; H, 3.91; N, 9.84. Calc. for $C_{27}H_{26}N_6O_{14}Cu_2.5H_2O$: C, 37.03; H, 4.14; N, 9.60 revealing a M_2L complex.

With copper perchlorate

Copper perchlorate (35.0mg, 0.094mmol) dissolved in methanol (5ml) was added to a solution of ligand **2.45** (19.3mg, 0.047mmol) dissolved in dichloromethane (5ml). A small amount of precipitate appeared at the boundary between the solutions. A few weeks later the purple precipitate was filtered off and dried *in vacuo*. Yield 16mg (31%). Anal. Found: C, 58.69; H, 4.80; N, 5.00. Calc. for $C_{54}H_{52}N_4O_{12}Cl_2Cu.H_2O$: C, 58.88; H, 4.94; N, 5.09 revealing a ML_2 complex.

With palladium chloride

Palladium chloride (18.6mg, 0.10mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **2.45** (20.2mg, 0.05mmol). Immediately the solution turned orange and an orange solid precipitated. A few weeks later the orange solid was filtered off and dried *in vacuo*. Yield 13.9mg (42%). M.p. 286-287°C. Anal. Found: C, 49.37; H, 4.78; N, 4.09. Calc. for $C_{27}H_{26}N_2O_2Cl_2Pd.4H_2O$: C, 49.14; H, 5.19; N, 4.25 revealing a 1:1 complex.

Complexes with 2.47

With zinc bromide, viz **2.50**

Zinc bromide (14.1mg, 0.063mmol) was dissolved in methanol (5ml) and layered upon a solution of ligand **2.47** (12.0mg, 0.029mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting reaction mixture gave colourless plate-like crystals of **2.50** that were suitable for X-ray crystallography and revealed a 1-dimensional polymer. Yield 14.2mg (76%). M.p. 270°C. Anal. Found: C, 50.72; H, 4.49; N, 4.33. Calc. for $C_{27}H_{26}N_2O_2Br_2Zn.⅓H_2O$: C, 50.54; H, 4.19; N, 4.37.

With copper(II) chloride

A solution of copper(II) chloride (17.0mg, 0.1mmol) dissolved in methanol (10ml) was layered upon a solution of ligand **2.47** (20.7mg, 0.05mmol) dissolved in hot methanol (10ml). A green precipitate formed immediately, which was collected by filtration a few weeks later and dried *in vacuo*. Yield 25.5mg (73%). M.p. 185-187°C. Anal. Found: C, 46.69; H, 4.17; N, 3.97. Calc. for $C_{27}H_{26}N_2O_2Cl_4Cu_2.H_2O$: C, 46.50; H, 4.05; N, 4.02 revealing a M_2L complex.

With copper(I) iodide

A solution of copper(I) iodide (19.7mg, 0.10mmol) dissolved in acetonitrile (10ml) was carefully layered onto a solution of ligand **2.47** (20.5mg, 0.05mmol) dissolved in dichloromethane (10ml). A small amount of yellow precipitate appeared at the boundary between the solutions. A few weeks later the yellow precipitate was filtered off. Yield 17.6mg (44.1%). M.p. 160-164°C. Anal. Found: C, 40.12; H, 3.24; N, 3.37. Calc. for $C_{27}H_{26}N_2O_2I_2Cu_2.½H_2O$: C, 40.52; H, 3.40; N, 3.50 revealing a M_2L complex.

With copper nitrate

Copper nitrate (25.6mg, 0.11mmol) and ligand **2.47** (20.6mg, 0.05mmol) were both dissolved in hot methanol, allowed to cool and combined. After a few weeks a turquoise blue precipitate formed. This was collected by filtration and dried *in vacuo*. Yield 33.7mg (79.6%). M.p. 207-211°C. Anal. Found: C, 38.01; H, 3.80; N, 9.67. Calc. for $C_{27}H_{26}N_6O_{14}Cu_2.3½H_2O$: C, 38.21; H, 3.92; N, 9.90 revealing a M_2L complex.

With palladium chloride

Palladium chloride (18.2mg, 0.10mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **2.47** (20.5mg, 0.05mmol). Immediately the solution turned orange and an orange solid precipitated. A few weeks later the orange solid was filtered off and dried *in vacuo*. Yield 14mg (44%). M.p. 199-201°C. Anal. Found: C, 50.78; H, 4.63; N, 4.27. Calc. for $C_{27}H_{26}N_2O_2Cl_2Pd.3H_2O$: C, 50.52; H, 5.02; N, 4.36 revealing a 1:1 complex.

Complexes with 2.49

With copper nitrate, viz **2.51**

To a hot solution of ligand **2.49** (20.5mg, 0.05mmol) dissolved in methanol (10ml), was added a solution of copper nitrate (26.4mg, 0.1mmol) also dissolved in hot methanol (10ml). On standing for a few weeks blue plate-like crystals formed on the sides of the vial. The blue crystals were filtered off and found to be suitable for X-ray crystallography revealing a 1:1 metal to ligand complex. Yield 8.6mg (20.1%). M.p. 208-210°C. Anal. Found: C, 37.41; H, 3.71; N, 9.70. Calc. for $C_{27}H_{26}N_6O_{14}Cu_2.4H_2O$: C, 37.81; H, 4.00; N, 9.80.

With copper(I) iodide

Copper(I) iodide (19.4mg, 0.10mmol) and ligand **2.49** (20.2mg, 0.05mmol) were both dissolved in hot acetonitrile (10ml) and combined. Slow evaporation of the resulting pale yellow solution produced an orange/yellow crystalline solid after a few months. This crystalline solid was filtered off and dried *in vacuo*. Yield 23.1mg (58.5%). M.p. 150-153°C. Anal. Found: C, 41.01; H, 3.33; N, 3.62. Calc. for $C_{27}H_{26}N_2O_2I_2Cu_2$: C, 40.98; H, 3.31; N, 3.54 revealing a M_2L complex

With palladium chloride

Palladium chloride (18.2mg, 0.10mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **2.49** (20.4mg, 0.05mmol). Immediately the solution turned orange and an orange solid precipitated. A few weeks later the orange solid was filtered off and dried *in vacuo*. Yield 9.2mg (29%). M.p. 280°C. Anal. Found:

C, 52.44; H, 5.04; N, 4.06. Calc. for $C_{27}H_{26}N_2O_2Cl_2Pd.H_2O.CH_3OH$: C, 52.72; H, 5.06; N, 4.39 revealing a 1:1 complex.

Preparation of complexes with the Bisphenol Z ligands

Complexes with 2.53

With cobalt(II) chloride, viz **2.61**

A solution of cobalt(II) chloride (22.0mg, 0.096mmol) dissolved in acetone (3ml) was layered upon a solution of ligand **2.53** (20.3mg, 0.048mmol) dissolved in 1:1 acetone:dichloromethane (3ml). A blue crystalline solid formed within minutes after mixing. Amongst the clusters of needle-like blue crystals were some blue crystalline plates which were suitable for X-ray crystallography. Yield 27.9mg (95.4%). M.p. 301-302°C. Anal. Found: C, 52.47; H, 4.98; N, 4.03. Calc. for $C_{28}H_{26}N_2O_2Cl_2Co.2H_2O.CH_2Cl_2.(CH_3)_2CO$: C, 52.55; H, 5.24; N, 3.83.

With copper(II) chloride, viz **2.62**

A solution of copper(II) chloride (21.3mg, 0.12mmol) dissolved in methanol (10ml) was layered upon a solution of ligand **2.53** (26.4mg, 0.062mmol) dissolved in dichloromethane (10ml). Slow evaporation of the resulting pale green solution gave blue rod-like crystals of **2.62** suitable for X-ray crystallography. Yield 30mg (82%). M.p. 189-190°C. Anal. Found: C, 59.30; H, 5.00; N, 4.60. Calc. for $C_{28}H_{26}N_2O_2Cl_2Cu.CH_3OH$: C, 59.13; H, 5.13; N, 4.76.

With zinc bromide, viz **2.63**

Zinc bromide (24.9mg, 0.11mmol) was dissolved in methanol (10ml) and layered upon a solution of ligand **2.53** (23.0mg, 0.054mmol) dissolved in dichloromethane (10ml). Slow evaporation of the resulting reaction mixture gave colourless plate-like crystals of **2.63** that were suitable for X-ray crystallography and revealed a 1-dimensional helical polymer. Yield 32.2mg (92.6%). M.p. 300-301°C. Anal. Found: C, 51.95; H, 4.05; N, 4.32. Calc. for $C_{28}H_{26}N_2O_2Br_2Zn$: C, 51.92; H, 4.05; N, 4.32.

With zinc chloride, viz **2.64**

Zinc chloride (20.4mg, 0.149mmol) was dissolved in methanol (5ml) and layered upon a solution of ligand **2.53** (27mg, 0.064mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting reaction mixture gave colourless plate-like crystals of **2.64** that were suitable for X-ray crystallography and revealed a 1-dimensional helical polymer. Yield 16.2mg (43.4%). M.p. 288°C. Anal. Found: C, 57.95; H, 4.68; N, 4.79. Calc. for $C_{28}H_{26}N_2O_2Cl_2Zn.⅓CH_3OH$: C, 57.96; H, 4.58; N, 4.77.

With copper(I) iodide

A solution of copper(I) iodide (25.2mg, 0.13mmol) dissolved in acetonitrile (10ml) was carefully layered onto a solution of ligand **2.53** (28.0mg, 0.066mmol) dissolved in dichloromethane (10ml). Slow evaporation of the resulting colourless solution produced a bronze coloured crystalline solid. This solid was filtered off and dried *in vacuo*. Yield 41mg (61.5%). M.p. 175-179°C. Anal. Found: C, 37.99; H, 3.17; N, 4.16. Calc. for $C_{28}H_{26}N_2O_2I_2Cu_2.2CH_2Cl_2.CH_3CN$: C, 37.89; H, 3.28; N, 4.14 revealing a M_2L complex.

With copper perchlorate

Copper perchlorate (60.9mg, 0.164mmol) dissolved in methanol (5ml) and added to a solution of ligand **2.53** (34.4mg, 0.081mmol) dissolved in dichloromethane (5ml). The solution turned blue and a fine blue precipitate formed on standing, which was collected by filtration, washed with methanol and dried *in vacuo*. Yield 25.1mg (39.9%). Anal. Found: C, 43.27; H, 4.59; N, 3.50. Calc. for $C_{28}H_{26}N_2O_{10}Cl_2Cu.5H_2O$: C, 43.39; H, 4.68; N, 3.61 revealing a 1:1 complex.

With silver hexafluorophosphate

Ligand **2.53** (22.1mg, 0.052mmol) was dissolved in chloroform (2ml) and overlaid with a solution of silver hexafluorophosphate (13.1mg, 0.052mmol). Slow evaporation and vapour diffusion of ether into the mixture gave a fine white precipitate. A few weeks later this white precipitate was filtered off. Yield 24.6mg (68.4%). M.p. 138-139°C. Anal. Found: C, 48.19; H, 4.23; N, 3.88. Calc. for $C_{28}H_{26}N_2O_2PF_6Ag.H_2O$: C, 48.50; H, 4.07; N, 4.04 revealing a 1:1 complex.

With silver perchlorate

Ligand **2.53** (22.0mg, 0.052mmol) was dissolved in chloroform (2ml) and silver perchlorate (21.6mg, 0.10mmol) was dissolved in acetone (3ml). The solutions were mixed together, and left to slowly evaporate with vapor diffusion of ether into the mixture. A crystalline material formed on standing, which was collected by filtration and dried *in vacuo*. Yield 32.4mg (74.7%). Anal. Found: C, 40.25; H, 3.64; N, 3.22. Calc. for $C_{28}H_{26}N_2O_{10}Cl_2Ag_2$: C, 40.17; H, 3.13; N, 3.35 revealing a M_2L complex.

Complexes with 2.54

With copper(I) iodide, viz **2.65**

A solution of copper(I) iodide (27.5mg, 0.14mmol) dissolved in acetonitrile (10ml) was carefully layered onto a solution of ligand **2.54** (30.7mg, 0.072mmol) dissolved in dichloromethane (10ml). Slow evaporation of the resulting yellow solution produced beautiful yellow block-like crystals suitable for X-ray crystallography. The X-ray analysis revealed a novel 'necklace' type structure. Yield 26.9mg (60.8%). M.p. 236-238.5°C. Anal. Found: C, 50.74; H, 4.07; N, 9.12. Calc. for $C_{26}H_{24}N_4O_2ICu$: C, 50.78; H, 3.93; N, 9.11.

With cobalt(II) bromide, viz **2.66**

A solution of cobalt(II) bromide (27.2mg, 0.12mmol) dissolved in acetone (3ml) was layered upon a solution of ligand **2.54** (24.6mg, 0.058mmol) dissolved in acetone (3ml). Slow evaporation of the resulting reaction mixture produced blue plate-like crystals of **2.66** that were suitable for X-ray crystallography and revealed a 1-dimensional necklace polymer chain. Yield 22.5mg (39%). M.p. 223-224°C. Anal. Found: C, 57.65; H, 4.70; N, 10.08. Calc. for $C_{52}H_{48}N_8O_4Br_2Co.H_2O$: C, 57.52; H, 4.64; N, 10.32.

With copper(II) chloride

A solution of copper(II) chloride (22.1mg, 0.013mmol) dissolved in methanol (10ml) was layered upon a solution of ligand **2.54** (27.5mg, 0.065mmol) dissolved in dichloromethane (10ml). Slow evaporation of the resulting green solution gave a green crystalline solid. A few weeks later this green crystalline solid was filtered off. Yield 38.2mg (70.5%). M.p. 180°C. Anal. Found: C, 39.03; H, 3.66; N, 6.80. Calc. for

$C_{26}H_{24}N_4O_2Cl_4Cu_2.H_2O.1½CH_2Cl_2$: C, 39.38; H, 3.48; N, 6.68 revealing a M_2L complex.

With silver hexafluorophosphate

A solution of ligand **2.54** (22.3mg, 0.053mmol) in chloroform (3ml) was layered upon a solution of silver hexafluorophosphate (12.6mg, 0.053mmol) dissolved in a solution of acetone (2ml). Immediately a white precipitate formed which was collected by filtration and dried *in vacuo*. Yield 25.2mg (70.3%). M.p. 252-257°C. Anal. Found: C, 45.97; H, 3.96; N, 7.99. Calc. for $C_{26}H_{24}N_4O_2PF_6Ag$: C, 46.10; H, 3.57; N, 8.27 revealing a 1:1 complex.

With silver perchlorate

A solution of ligand **2.54** (23.2mg, 0.055mmol) in chloroform (3ml) was layered upon a solution of silver perchlorate (11.3mg, 0.055mmol) dissolved in acetone (2ml). Immediately a crystalline material formed which was collected by filtration and dried *in vacuo*. Yield 24.6mg (68.1%). Anal. Found: C, 47.36; H, 3.96; N, 8.29. Calc. for $C_{26}H_{24}N_4O_6ClAg.1½H_2O$: C, 47.40; H, 4.13; N, 8.50 revealing a 1:1 complex.

With silver trifluoromethanesulfonate

A solution of ligand **2.54** (25.1mg, 0.06mmol) in hot acetone (3ml) was layered upon a solution of silver trifluoromethanesulfonate (15.7mg, 0.06mmol) also dissolved in acetone (2ml). Immediately a white precipitate formed which was collected by filtration and dried *in vacuo*. Yield 20.6mg (48.6%). M.p. 235-240°C. Anal. Found: C, 45.99; H, 3.63; N, 7.54. Calc. for $C_{27}H_{24}N_4O_6F_3SAg.1½H_2O$: C, 45.77; H, 3.84; N, 7.91 revealing a 1:1 complex.

Complexes with 2.55

With copper(II) chloride

A solution of copper(II) chloride (12.1mg, 0.071mmol) dissolved in methanol (10ml) was layered upon a solution of ligand **2.55** (18.6mg, 0.036mmol) dissolved in dichloromethane (10ml). Slow evaporation of the resulting pale green solution gave a

green crystalline solid. A few weeks later this green crystalline solid was filtered off. Yield 23.2mg (80%). M.p. 229-231°C. Anal. Found: C, 53.69; H, 4.49; N, 3.49. Calc. for $C_{36}H_{30}N_2O_2Cl_4Cu_2.H_2O$: C, 53.41; H, 3.98; N, 3.46 revealing a M_2L complex.

With silver hexafluorophosphate

A solution of ligand **2.55** (21.7mg, 0.042mmol) in chloroform (3ml) was layered upon a solution of silver hexafluorophosphate (10.6mg, 0.042mmol) dissolved in acetone (2ml). Slow evaporation of the resulting colourless solution and vapour diffusion of ether, gave a colourless crystalline material. A few weeks later this was collected by filtration and dried *in vacuo*. Yield 25.5mg (23.6%). M.p. 215-217°C. Anal. Found: C, 49.96; H, 3.99; N, 3.28. Calc. for $C_{108}H_{90}N_6O_6P_4F_{24}Ag_4$: C, 50.29; H, 3.52; N, 3.26 revealing a M_4L_3 complex.

With silver perchlorate

Ligand **2.55** (17.2mg, 0.033mmol) was dissolved in chloroform (2ml) and silver perchlorate (7.0mg, 0.033mmol) was dissolved in acetone (3ml). The solutions were mixed together, and left to slowly evaporate with vapor diffusion of ether into the mixture. A brown precipitate formed on standing, which was collected by filtration and dried *in vacuo*. Yield 23.9mg (82%). Anal. Found: C, 50.54; H, 4.08; N, 3.41. Calc. for $C_{36}H_{30}N_2O_6ClAg$: C, 50.19; H, 3.98; N, 3.16 revealing a 1:1 complex.

With silver tetrafluoroborate

A solution of ligand **2.55** (10.5mg, 0.020mmol) in chloroform (3ml) was layered upon a solution of silver tetrafluoroborate (5.6mg, 0.028mmol) dissolved in acetone (2ml). Slow evaporation of the resulting colourless solution and vapour diffusion of ether, gave a colourless crystalline material. A few weeks later this was collected by filtration and dried *in vacuo*. Yield 11.5mg (75%). M.p. 230-231°C. Anal. Found: C, 56.83; H, 4.06; N, 3.58. Calc. for $C_{36}H_{30}N_2O_2BF_4Ag.2½H_2O$: C, 56.72; H, 4.63; N, 3.67 revealing a 1:1 complex.

Complexes with 2.56

With silver hexafluorophosphate

Ligand **2.56** (18.0mg, 0.034mmol) was dissolved in chloroform (2ml) and overlaid with a solution of silver hexafluorophosphate (8.6mg, 0.034mmol) in acetone. The solutions were mixed together, and left to slowly evaporate with vapor diffusion of ether into the mixture. A yellow solid formed within minutes of mixing, which was collected by filtration and dried *in vacuo.* Yield 13.2mg (40%). M.p. 180-181°C. Anal. Found: C, 49.81; H, 4.23; N, 5.99. Calc. for $C_{34}H_{28}N_4O_2PF_6Ag.2(CH_3)_2CO.⅔CHCl_3$: C, 50.19; H, 4.21; N, 5.76 revealing a 1:1 complex.

With silver perchlorate

Ligand **2.56** (17.5mg, 0.033mmol) was dissolved in chloroform (2ml) and silver perchlorate (6.90mg, 0.033mmol) was dissolved in acetone (3ml). The solutions were mixed together, and left to slowly evaporate with vapor diffusion of ether into the mixture. A yellow solid formed within minutes of mixing, which was collected by filtration and dried *in vacuo*. Yield 15.8mg (62%). Anal. Found: C, 53.19; H, 4.44; N, 6.69. Calc. for $C_{34}H_{28}N_4O_6ClAg.2H_2O$: C, 53.18; H, 4.20; N, 7.30 revealing a 1:1 complex.

With silver tetrafluoroborate

Ligand **2.56** (16.9mg, 0.032mmol) was dissolved in chloroform (2ml) and silver tetrafluoroborate (6.3mg, 0.0.032mmol) was dissolved in acetone (3ml). The solutions were mixed together, and left to slowly evaporate with vapor diffusion of ether into the mixture. A pale yellow solid formed within minutes of mixing, which was collected by filtration and dried *in vacuo*. Yield 19.4mg (59%). M.p. 240-245°C. Anal. Found: C, 46.92; H, 3.90; N, 5.83. Calc. for $C_{34}H_{28}N_4O_2B_2F_8Ag_2.2(CH_3)_2CO$: C, 46.64; H, 3.91; N, 5.44 revealing a M_2L complex.

Complexes with 2.67

With cobalt(II) bromide

A solution of cobalt(II) bromide (9.5mg, 0.043mmol) dissolved in acetone (3ml) was layered upon a solution of ligand **2.67** (8.2mg, 0.018mmol) dissolved in chloroform (3ml). Slow evaporation gave a blue crystalline solid, which was filtered off. Yield 7.1mg (55.5%). M.p. 252°C. Anal. Found: C, 51.32; H, 4.48; N, 3.88. Calc. for $C_{30}H_{30}N_2O_2Br_2Co.2H_2O$: C, 51.08; H, 4.86; N, 3.97 revealing a 1:1 complex.

With silver perchlorate

A solution of ligand **2.67** (9.3mg, 0.021mmol) in chloroform (2ml) was layered upon a solution of silver perchlorate (4.2mg, 0.021mmol) dissolved in acetone (2ml). A crystalline precipitate formed immediately which was filtered off and dried *in vacuo*. Yield 5.1mg (37.6%). M.p. 217-218°C. Anal. Found: C, 54.78; H, 4.77; N, 4.10. Calc. for $C_{30}H_{30}N_2O_6ClAg$: C, 54.77; H, 4.60; N, 4.26 revealing a 1:1 complex.

With silver hexafluorophosphate

A solution of ligand **2.67** (10mg, 0.022mmol) in chloroform (2ml) was layered upon a solution of silver hexafluorophosphate (7mg, 0.021mmol) dissolved in acetone (2ml). A crystalline precipitate formed immediately which was filtered off and dried *in vacuo*. Yield 6.1mg (42%). M.p. 220-222°C. Anal. Found: C, 51.22; H, 4.49; N, 4.01. Calc. for $C_{30}H_{30}N_2O_2PF_6Ag$: C, 51.23; H, 4.30; N, 3.98 revealing a 1:1 complex.

With zinc bromide

Zinc bromide (8.2mg, 0.036mmol) dissolved in methanol (5ml) was added to a solution of ligand **2.67** (10mg, 0.022mmol) dissolved in dichloromethane (5ml). The solution immediately went cloudy. A few weeks later a crystalline solid was filtered off and dried *in vacuo*. Yield 8.7mg (57.5%). M.p. 215-216°C. Anal. Found: C, 52.57; H, 4.49; N, 3.95. Calc. for $C_{30}H_{30}N_2O_2Br_2Zn.½H_2O$: C, 52.62; H, 4.56; N, 4.09 revealing a 1:1 complex.

Complexes with 2.68

With zinc chloride, viz **2.70**

A solution of zinc chloride (17mg, 0.124mmol) in methanol (5ml) was layered upon a solution of ligand **2.68** (26.9mg, 0.059mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting solution gave colourless plate-like crystals of **2.70** suitable for X-ray crystallography which revealed a [2+2] macrocycle. Yield 19.8mg (26.2%). M.p. 200°C. Anal. Found: C, 59.81; H, 5.07; N, 4.61. Calc. for $C_{30}H_{30}N_2O_2Cl_2Zn.H_2O$: C, 59.57; H, 5.33; N, 4.63.

With silver perchlorate

A solution of ligand **2.68** (20.7mg, 0.046mmol) in chloroform (2ml) was layered upon a solution of silver perchlorate (10.8mg, 0.052mmol) dissolved in acetone (2ml). A crystalline precipitate formed immediately which was filtered off and dried *in vacuo*. Yield 19mg (62%). M.p. 257-260°C. Anal. Found: C, 53.90; H, 4.49; N, 4.02. Calc. for $C_{30}H_{30}N_2O_6ClAg.½H_2O$: C, 54.03; H, 4.69; N, 4.20 revealing a 1:1 complex.

With silver hexafluorophosphate

A solution of ligand **2.68** (22.7mg, 0.050mmol) in chloroform (2ml) was layered upon a solution of silver hexafluorophosphate (13.8mg, 0.054mmol) dissolved in acetone (2ml). A crystalline precipitate formed immediately which was filtered off and dried *in vacuo*. Yield 20.7mg (54%). M.p. 218-222°C. Anal. Found: C, 52.53; H, 4.45; N, 4.06. Calc. for $C_{30}H_{30}N_2O_2PF_6Ag.(CH_3)_2CO$: C, 52.05; H, 4.77; N, 3.68 revealing a 1:1 complex.

With zinc bromide

Zinc bromide (27.8mg, 0.123mmol) dissolved in methanol (5ml) was added to a solution of ligand **2.68** (27.7mg, 0.062mmol) dissolved in dichloromethane (5ml). Immediately a green precipitate formed. A few weeks later the colourless crystalline solid was filtered off and dried *in vacuo*. Yield 30.5mg (70.9%). M.p. 242°C. Anal. Found: C, 51.15; H, 4.25; N, 3.83. Calc. for $C_{30}H_{30}N_2O_2Br_2Zn.1½H_2O$: C, 51.27; H, 4.73; N, 3.99 revealing a 1:1 complex.

Complexes with 2.69

With copper(I) iodide, viz **2.71**

A solution of copper(I) iodide (19.5mg, 0.10mmol) dissolved in acetonitrile (10ml) was carefully layered onto a solution of ligand **2.69** (22.5mg, 0.05mmol) dissolved in dichloromethane (10ml). Slow evaporation of the resulting yellow solution produced yellow block-like crystals suitable for X-ray crystallography. Yield 11.7mg (35.4%). M.p. 175-176°C. Anal. Found: C, 54.65; H, 4.88; N, 4.86. Calc. for $C_{30}H_{30}N_2O_2ICu.¼CH_2Cl_2$: C, 54.96; H, 4.64; N, 4.23.

With copper nitrate, viz **2.72**

To a hot solution of ligand **2.69** (20.5mg, 0.05mmol) dissolved in methanol (10ml), was added a solution of copper nitrate (25.8mg, 0.11mmol) dissolved in dichloromethane (10ml). After a week a few single blue crystals grew on the bottom of the vial that were suitable for X-ray crystallography which revealed a 2:1 metal to ligand complex. However, due to the lack of material no further analysis could be carried out. Yield 3.3mg.

With zinc bromide, viz **2.73**

A solution of zinc bromide (23.9mg, 0.11mmol) in methanol (10ml) was layered upon a solution of ligand **2.69** (22.5mg, 0.05mmol) dissolved in dichloromethane (10ml). Slow evaporation of the resulting solution gave colourless block-like crystals of **2.73** suitable for X-ray crystallography, which gave a 1-dimensional helical polymer. Yield 23.5mg (68.3%). M.p. 270-275°C. Anal. Found: C, 53.33; H, 4.35; N, 3.90. Calc. for $C_{30}H_{30}N_2O_2Br_2Zn.½CH_3OH$: C, 52.95; H, 4.66; N, 4.05.

With zinc chloride, viz **2.74**

A solution of zinc chloride (12.6mg, 0.092mmol) in methanol (5ml) was layered upon a solution of ligand **2.69** (20.2mg, 0.045mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting solution gave colourless plate-like crystals suitable for X-ray crystallography, which showed a 1-dimensional helical polymer. Yield 19.9mg (75.9%). M.p. 254-256°C. Anal. Found: C, 61.31; H, 4.87; N, 4.73. Calc. for $C_{30}H_{30}N_2O_2Cl_2Zn$: C, 61.40; H, 5.14; N, 4.77.

With copper(II) chloride

A solution of copper(II) chloride (18.4mg, 0.1mmol) dissolved in methanol (5ml) was layered upon a solution of ligand **2.69** (21.7mg, 0.05mmol) dissolved in hot methanol (5ml). The solution turned green and a green solid formed on slow evaporation. A few weeks later the green solid was filtered off and dried *in vacuo*. Yield 24.8mg (62.9%). M.p. 165-170°C. Anal. Found: C, 45.84; H, 4.46; N, 3.65. Calc. for $C_{30}H_{30}N_2O_2Cl_4Cu_2.4H_2O$: C, 45.52; H, 4.84; N, 3.54 revealing a M_2L complex.

With palladium chloride

Palladium chloride (18.2mg, 0.10mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **2.69** (22.5mg, 0.05mmol). Immediately the solution turned orange and an orange solid precipitated. A few weeks later the orange solid was filtered off and dried *in vacuo*. Yield 23.6mg (68%). M.p. 225-226°C. Anal. Found: C, 53.72; H, 5.10; N, 4.01. Calc. for $C_{30}H_{30}N_2O_2Cl_2Pd.2H_2O.CH_3OH$: C, 53.50; H, 5.50; N, 4.03 revealing a 1:1 complex.

Preparation of complexes with the Bisphenol AP ligands

Complexes with 3.2

With silver hexafluorophosphate, viz **3.8**

Ligand **3.2** (24.5mg, 0.055mmol) was dissolved in chloroform (2ml) and layered upon a solution of silver hexafluorophosphate (13.9mg, 0.055mmol) dissolved in acetone (2ml). Slow evaporation and vapour diffusion of diethyl ether into the reaction mixture gave colourless plate-like crystals of **3.8** suitable for X-ray crystallography revealing a M_2L_2 macrocycle. Yield 22.7mg (59.3%). M.p. 200-204°C. Anal. Found: C, 51.85; H, 4.03; N, 3.77. Calc. for $C_{30}H_{24}N_2O_2PF_6Ag$: C, 51.67; H, 3.47; N, 4.02.

With cobalt(II) chloride

A solution of cobalt(II) chloride (21.8mg, 0.092mmol) was dissolved in acetone (3ml) was layered upon a solution of ligand **3.2** (20.6mg, 0.046mmol) dissolved in hot acetone (3ml). The resulting blue solution was concentrated by slow evaporation to give

a blue crystalline solid that was collected by filtration and dried *in vacuo*. Yield 25.4mg (74.6%). M.p. 288-291°C. Anal. Found: C, 51.13; H, 4.14; N, 3.83. Calc. for $C_{30}H_{24}N_2O_2Cl_4Co_2.½(CH_3)_2CO.½H_2O$: C, 50.97; H, 3.80; N, 3.77 revealing a M_2L complex.

With copper perchlorate

Copper perchlorate (64.6mg, 0.174mmol) dissolved in methanol (5ml) was added to a solution of ligand **3.2** (35.2mg, 0.079mmol) dissolved in dichloromethane (5ml). The solution turned blue and a fine blue crystalline precipitate formed on standing, which was collected by filtration and dried *in vacuo*. Yield 33.1mg (21.8%). Anal. Found: C, 55.95; H, 4.06; N, 4.36. Calc. for $C_{90}H_{72}N_6O_{22}Cl_4Cu_2.4H_2O$: C, 55.99; H, 4.18; N, 4.35 revealing a M_2L_3 complex.

With silver perchlorate

Ligand **3.2** (22.0mg, 0.049mmol) was dissolved in chloroform (2ml) and silver perchlorate (10.2mg, 0.049mmol) was dissolved in acetone (3ml). The solutions were mixed together, and left to slowly evaporate with vapor diffusion of ether into the mixture. A white solid formed on standing, which was collected by filtration and dried *in vacuo*. Yield 6.9mg (20.5%). Anal. Found: C, 52.64; H, 3.81; N, 3.92. Calc. for $C_{30}H_{24}N_2O_6ClAg.2H_2O$: C, 52.38; H, 4.10; N, 4.07 revealing a 1:1 complex.

With silver trifluoromethanesulfonate

A solution of ligand **3.2** (30.5mg, 0.068mmol) in chloroform (3ml) was layered upon a solution of silver trifluoromethanesulfonate (17.6mg, 0.068mmol) dissolved in acetone (2ml). Slow evaporation of the resulting colourless solution and vapour diffusion of ether gave a colourless crystalline material. The crystalline solid was collected by filtration and dried *in vacuo*. Yield 24.3mg (23.5%). M.p. 219-221°C. Anal. Found: C, 49.40; H, 3.25; N, 3.55. Calc. for $C_{62}H_{48}N_4O_{10}F_6S_2Ag3$: C, 49.29; H, 3.20; N, 3.71 revealing a M_3L_2 complex.

Complexes with 3.3

With copper(I) iodide

Copper(I) iodide (21.9mg, 0.12mmol) and ligand **3.3** (25.7mg, 0.06mmol) were both dissolved in hot acetonitrile (10ml), the solutions combined and left to stand. Vapour diffusion of ether into this solution gave a pale orange crystalline precipitate that was collected by filtration. Yield 33.5mg (85.3%). Anal. Found: C, 51.28; H, 3.57; N, 8.78. Calc. for $C_{28}H_{22}N_4O_2ICu.H_2O$: C, 51.35; H, 3.69; N, 8.55 revealing a 1:1 complex.

With silver hexafluorophosphate

A solution of ligand **3.3** (19.3mg, 0.04mmol) in chloroform (3ml) was layered upon a solution of silver hexafluorophosphate (10.9mg, 0.04mmol) dissolved in acetone (2ml). Immediately a precipitate formed. The pale brown precipitate was collected by filtration and dried *in vacuo*. Yield 17.5mg (49%). M.p. 169-171°C. Anal. Found: C, 44.29; H, 3.52; N, 6.69. Calc. for $C_{28}H_{22}N_4O_2PF_6Ag.CHCl_3.1⅓(CH_3)_2CO$: C, 44.23; H, 3.49; N, 6.25 revealing a 1:1 complex.

With silver perchlorate

A solution of ligand **3.3** (23.9mg, 0.05mmol) in chloroform (3ml) was layered upon a solution of silver perchlorate (11.0mg, 0.05mmol) dissolved in acetone (2ml). Immediately a crystalline solid formed which was collected by filtration a few weeks later and dried *in vacuo*. Yield 24.5mg (67.5%). Anal. Found: C, 48.08; H, 3.71; N, 7.27. Calc. for $C_{28}H_{22}N_4O_6ClAg.½CHCl_3.½H_2O$: C, 48.26; H, 3.32; N, 7.70 revealing a 1:1 complex.

With silver trifluoromethanesulfonate

A solution of ligand **3.3** (21.9mg, 0.049mmol) in chloroform (3ml) was layered upon a solution of silver trifluoromethanesulfonate (12.6mg, 0.049mmol) dissolved in acetone (2ml). Immediately a white precipitate formed which was collected and dried *in vacuo*. Yield 23.8mg (62.8%). M.p. 155-157°C. Anal. Found: C, 46.04; H, 3.58; N, 6.88. Calc. for $C_{29}H_{22}N_4O_5F_3SAg.3/5CHCl_3$: C, 45.87; H, 2.94; N, 7.23 revealing a 1:1 complex.

Complexes with 3.4

With silver perchlorate

Ligand **3.4** (18.5mg, 0.034mmol) was dissolved in chloroform (2ml) and silver perchlorate (7.9mg, 0.038mmol) was dissolved in acetone (3ml). The solutions were mixed together, and left to slowly evaporate with vapor diffusion of ether into the mixture. A white precipitate formed within minutes of mixing, which was collected by filtration and dried *in vacuo*. Yield 13.7mg (51.3%). M.p. 217-220°C. Anal. Found: C, 57.40; H, 3.63; N, 3.46. Calc. for $C_{38}H_{28}N_2O_6ClAg.2H_2O$: C, 57.92; H, 4.09; N, 3.56 revealing a 1:1 complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (43.7mg, 0.115mmol) in acetone (6ml) was layered upon a solution of ligand **3.4** (30.9mg, 0.057mmol) dissolved in hot acetone (5ml). Immediately a brown crystalline precipitate formed which was collected by filtration and dried *in vacuo*. Yield 29.9mg (31.2%). M.p. 293-294°C. Anal. Found: C, 53.55; H, 3.63; N, 3.68. Calc. for $C_{76}H_{56}N_4O_4Cl_6Pd_3.4H_2O$: C, 53.91; H, 3.81; N, 3.31 revealing a M_3L_2 complex.

With zinc bromide

A solution of zinc bromide (21.9mg, 0.097mmol) dissolved in methanol (10ml) was layered upon a solution of ligand **3.4** (24.8mg, 0.046mmol) dissolved in dichloromethane (10ml). On standing a colourless crystalline solid precipitated from the reaction mixture. A few weeks later this crystalline solid was filtered off. Yield 10.3mg (41.5%). M.p. 178-180°C.

Complexes with 3.5

With silver perchlorate

A solution of ligand **3.5** (10.4mg, 0.018mmol) in chloroform (2ml) was layered upon a solution of silver perchlorate (3.7mg, 0.018mmol) dissolved in acetone (2ml). A white precipitate formed immediately which was filtered off and dried *in vacuo*. Yield 3.1mg

(9.3%). Anal. Found: C, 49.53; H, 3.34; N, 6.17. Calc. for $C_{76}H_{60}N_8O_{16}Cl_3Ag_3.⅔CHCl_3$: C, 49.75; H, 3.30; N, 6.05 revealing a M_3L_2 complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (29.0mg, 0.076mmol) in acetone (6ml) was layered upon a solution of ligand **3.5** (22.0mg, 0.038mmol) dissolved in hot acetone (5ml). Immediately a bronze coloured crystalline precipitate formed which was collected by filtration and dried *in vacuo*. Yield 22.1mg (57.8%). M.p. 281-282°C. Anal. Found: C, 45.48; H, 3.12; N, 5.35. Calc. for $C_{38}H_{30}N_4O_2Cl_4Pd_2.4H_2O$: C, 45.58; H, 3.82; N, 5.59 revealing a M_2L complex.

Complexes with 3.9

With cobalt(II) chloride

A solution of cobalt(II) chloride (20.5mg, 0.086mmol) dissolved in acetone (3ml) was layered upon a solution of ligand **3.9** (20.5mg, 0.043mmol) dissolved in hot acetone (3ml). Immediately a blue solid precipitated, which was collected by filtration and dried *in vacuo*. Yield 18.9mg (55.7%). M.p. 261-264°C. Anal. Found: C, 53.28; H, 4.67; N, 3.91. Calc. for $C_{32}H_{28}N_2O_2Cl_4Co_2.(CH_3)_2CO$: C, 53.19; H, 4.34; N, 3.54 revealing a M_2L complex.

With copper(II) chloride

A solution of copper(II) chloride (14.3mg, 0.084mmol) dissolved in methanol (10ml) was layered upon a solution of ligand **3.9** (19.1mg, 0.040mmol) dissolved in dichloromethane (10ml). Immediately a green precipitate formed which was collected by filtration and dried *in vacuo*. Yield 15.6mg (58.5%). M.p. 188-190°C. Anal. Found: C, 57.92; H, 4.28; N, 4.21. Calc. for $C_{32}H_{28}N_2O_2Cl_2Cu.3H_2O$: C, 58.14; H, 5.18; N, 4.24 revealing a 1:1 complex.

With copper(I) iodide

A solution of copper(I) iodide (18.9mg, 0.099mmol) dissolved in acetonitrile (10ml) was carefully layered onto a solution of ligand **3.9** (22.6mg, 0.048mmol) dissolved in

dichloromethane (10ml). A small amount of precipitate appeared at the boundary between the two solutions. A few weeks later the yellow precipitate was filtered off. Yield 14.6mg (35.8%). M.p. 220°C. Anal. Found: C, 45.43; H, 3.44; N, 3.47. Calc. for $C_{32}H_{28}N_2O_2I_2Cu_2$: C, 45.03; H, 3.31; N, 3.28 revealing a M_2L complex.

With copper perchlorate

Copper perchlorate (57.2mg, 0.154mmol) dissolved in methanol (5ml) was added to a solution of ligand **3.9** (35.8mg, 0.076mmol) dissolved in dichloromethane (5ml). A small amount of precipitate appeared at the boundary between the two solutions. A few weeks later the dark blue crystalline precipitate was filtered off. Yield 32mg (56.2%). Anal. Found: C, 51.13; H, 4.37; N, 3.75. Calc. for $C_{32}H_{28}N_2O_{10}Cl_2Cu_2.H_2O$: C, 51.04; H, 4.02; N, 3.72 revealing a 1:1 complex.

With silver perchlorate

A solution of ligand **3.9** (20.2mg, 0.043mmol) in chloroform (2ml) was layered upon a solution of silver perchlorate (8.7mg, 0.042mmol) dissolved in acetone (2ml). A white precipitate formed immediately which was filtered off and dried *in vacuo*. Yield 14.7mg (49.4%). M.p. 195°C. Anal. Found: C, 55.37; H, 4.25; N, 4.19. Calc. for $C_{32}H_{28}N_2O_6ClAg.H_2O$: C, 55.07; H, 4.33; N, 4.01 revealing a 1:1 complex.

Complexes with 3.10

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (64.9mg, 0.17mmol) in acetone (6ml) was layered upon a solution of ligand **3.10** (39.2mg, 0.083mmol) dissolved in hot acetone (5ml). Immediately an orange precipitate formed which was collected and dried *in vacuo*. Yield 29mg (16.4%). M.p. >138°C. Anal. Found: C, 54.03; H, 4.10; N, 4.49. Calc. for $C_{97}H_{88}N_6O_6Cl_8Pd_4$: C, 54.36; H, 4.14; N, 3.92 revealing a M_4L_3 complex.

With palladium chloride

Palladium chloride (17.6mg, 0.099mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **3.10** (22.4mg, 0.047mmol). Immediately the

solution went cloudy and a yellow precipitate began to form. A few weeks later the yellow precipitate was filtered off and dried *in vacuo*. Yield 20.5mg (62.4%). M.p. 251-255°C. Anal. Found: C, 55.26; H, 4.50; N, 3.94. Calc. for $C_{32}H_{28}N_2O_2Cl_2Pd.2½H_2O$: C, 55.31; H, 4.79; N, 4.03 revealing a 1:1 complex.

Complexes with 3.11

With copper(I) iodide

A solution of copper(I) iodide (23.3mg, 0.122mmol) dissolved in acetonitrile (5ml) was carefully layered onto a solution of ligand **3.11** (28.0mg, 0.059mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting colourless solution produced a yellow solid. This solid was filtered off and dried *in vacuo*. Yield 9.9mg (19.4%). M.p. 193-195°C. Anal. Found: C, 44.51; H, 3.62; N, 3.21. Calc. for $C_{32}H_{28}N_2O_2I_2Cu_2.½H_2O$: C, 44.56; H, 3.39; N, 3.25 revealing a M_2L complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (70.2mg, 0.18mmol) in acetone (6ml) was layered upon a solution of ligand **3.11** (43.3mg, 0.092mmol) dissolved in hot acetone (5ml). Immediately an orange precipitate formed which was collected and dried *in vacuo*. Yield 38.1mg (57.7%). M.p. 185-186°C. Anal. Found: C, 53.02; H, 5.20; N, 4.08. Calc. for $C_{32}H_{28}N_2O_2Cl_2Pd.4H_2O$: C, 53.24; H, 5.03; N, 3.88 revealing a 1:1 complex.

With palladium chloride

Palladium chloride (33.2mg, 0.187mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **3.11** (44.1mg, 0.093mmol). Immediately the solution went cloudy and a yellow precipitate began to form. A few weeks later the yellow precipitate was filtered off and dried *in vacuo*. Yield 45.6mg (69.6%). M.p. 225-228°C. Anal. Found: C, 55.57; H, 4.52; N, 3.90. Calc. for $C_{32}H_{28}N_2O_2Cl_2Pd.2½H_2O$: C, 55.53; H, 5.02; N, 3.99 revealing a 1:1 complex.

With silver perchlorate

A solution of ligand **3.11** (26.1mg, 0.055mmol) in chloroform (2ml) was layered upon a solution of silver perchlorate (13mg, 0.063mmol) dissolved in acetone (2ml). Slow evaporation of the resulting colourless solution and vapour diffusion of ether gave a crystalline precipitate on standing. A few weeks later the crystalline precipitate was collected by filtration and dried *in vacuo*. Yield 20.1mg (51.6%). M.p. 174-175°C. Anal. Found: C, 54.37; H, 4.32; N, 3.93. Calc. for $C_{32}H_{28}N_2O_6ClAg.1½H_2O$: C, 54.37; H, 4.42; N, 3.96 revealing a 1:1 complex.

With silver hexafluorophosphate

A solution of ligand **3.11** (25.3mg, 0.054mmol) in chloroform (2ml) was layered upon a solution of silver hexafluorophosphate (13mg, 0.051mmol) dissolved in acetone (2ml). Slow evaporation of the resulting colourless solution and vapour diffusion of ether gave a crystalline precipitate on standing. A few weeks later the crystalline precipitate was collected by filtration and dried *in vacuo*. Yield 3.2mg (7.7%). Anal. Found: C, 49.52; H, 4.12; N, 3.46. Calc. for $C_{32}H_{28}N_2O_2PF_6Ag.3H_2O$: C, 49.31; H, 4.40; N, 3.59 revealing a 1:1 complex.

Preparation of complexes with the 1,1,1-tris(4-hydroxyphenyl)ethane ligands

Complexes with 4.15

With copper(II) chloride, viz **4.22**

Copper(II) chloride (34mg, 0.199mmol) dissolved in methanol (5ml) was added to a solution of ligand **4.15** (30mg, 0.055mmol) dissolved in chloroform (5ml). Slow evaporation of the resulting solution gave large blue-green plate-like crystals suitable for X-ray crystallography. X-ray analysis revealed a M_3L_2 cage. Yield 31.1mg (35.7%). M.p. 240-242°C. Anal. Found: C, 54.06; H, 3.84; N, 5.41. Calc. for $C_{70}H_{54}N_6O_6Cl_6Cu_3.¾CHCl_3$: C, 54.19; H, 3.52; N, 5.36.

With copper(II) chloride, viz 7.148.1a

A solution of copper(II) chloride (28.5mg, 0.167mmol) dissolved in methanol (5ml) was layered upon a solution of ligand **4.15** (29.1mg, 0.054mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting solution gave blue-green plate-like crystals. Yield 17.8mg (21.8%). M.p. 218-219°C. Anal. Found: C, 55.30; H, 3.72; N, 5.52. Calc. for $C_{70}H_{54}N_6O_6Cl_6Cu_3.2H_2O$: C, 55.51; H, 3.86; N, 5.55.

With copper nitrate

A solution of copper nitrate (36.9mg, 0.153mmol) dissolved in methanol (10ml) was layered upon a solution of ligand **4.15** (27.5mg, 0.051mmol) dissolved in dichloromethane (10ml). Slow evaporation of the resulting pale blue solution produced a blue precipitate, which was filtered off and dried *in vacuo*. Yield 47.9mg (80%). M.p. 138-141°C. Anal. Found: C, 37.43; H, 3.13; N, 10.48. Calc. for $C_{35}H_{27}N_9O_{21}Cu_3.H_2O.2CH_3OH$: C, 37.59; H, 3.15; N, 10.66 revealing a M_3L complex.

With silver hexafluorophosphate

A solution of ligand **4.15** (25.8mg, 0.047mmol) in chloroform (3ml) was layered upon a solution of silver hexafluorophosphate (12.1mg, 0.047mmol) dissolved in acetone (2ml). Slow evaporation of the resulting colourless solution and vapour diffusion of ether, gave a colourless crystalline material. The silver complex was not able to be identified by X-ray crystallography, because the crystals were very fine needles that were extremely air sensitive and brittle. A few weeks later this crystalline material was filtered off and dried *in vacuo*. Yield 22.1mg (17.3%). M.p. 140-142°C. Anal. Found: C, 52.32; H, 4.07; N, 4.71. Calc. for $C_{35}H_{27}N_3O_3PF_6Ag.⅓CHCl_3.1⅓(CH_3)_2CO$: C, 52.05; H, 3.92; N, 4.63 revealing a 1:1 complex.

With silver perchlorate

A solution of ligand **4.15** (22.4mg, 0.042mmol) in chloroform (3ml) was layered upon a solution of silver perchlorate (8.6mg, 0.042mmol) dissolved in acetone (2ml). Slow evaporation of the resulting colourless solution and vapour diffusion of ether, gave a colourless crystalline material. The silver complex was not identified by X-ray crystallography, because the crystals were very fine needles that were extremely air sensitive and brittle. A few weeks later this crystalline material was collected by

filtration and dried *in vacuo*. Yield 20.2mg (58.5%). Anal. Found: C, 52.06; H, 3.72; N, 4.88. Calc. for $C_{35}H_{27}N_3O_7ClAg.\frac{2}{3}CHCl_3$: C, 51.96; H, 3.38; N, 5.10 revealing a 1:1 complex.

With silver trifluoromethanesulfonate

A solution of ligand **4.15** (23.3mg, 0.043mmol) in chloroform (3ml) was layered upon a solution of silver trifluoromethanesulfonate (11.1mg, 0.043mmol) dissolved in acetone (2ml). Slow evaporation of the resulting colourless solution and vapour diffusion of ether gave a colourless crystalline material. The crystalline solid was collected by filtration and dried *in vacuo*. Yield 15.4mg (43.5%). M.p. 189-192°C. Anal. Found: C, 52.93; H, 3.70; N, 4.90. Calc. for $C_{36}H_{27}N_3O_6F_3SAg.\frac{1}{4}CHCl_3$: C, 52.81; H, 3.33; N, 5.10 revealing a 1:1 complex.

With zinc bromide

A solution of zinc bromide (33.7mg, 0.15mmol) dissolved in methanol (10ml) was layered upon a solution of ligand **4.15** (25.8mg, 0.05mmol) dissolved in dichloromethane (10ml). On standing a colourless crystalline solid precipitated from the reaction mixture. A few weeks later this crystalline solid was filtered off. Yield 22.6mg (23.6%). M.p. 260-269°C. Anal. Found: C, 45.37; H, 3.40; N, 4.41. Calc. for $C_{69}H_{53}N_6O_6Br_6Zn_3.2CH_2Cl_2$: C, 45.02; H, 3.04; N, 4.38 revealing a M_3L_2 complex.

Complexes with 4.16

With copper(I) iodide, viz **4.23**

A solution of copper(I) iodide (22.9mg, 0.12mmol) dissolved in acetonitrile (10ml) was carefully layered onto a solution of ligand **4.16** (21.9mg, 0.04mmol) also dissolved in acetonitrile (10ml). Slow evaporation of the resulting yellow solution produced yellow plate-like crystals suitable for X-ray crystallography. The X-ray analysis revealed a double chain complex. Yield 25.8mg (75.8%). M.p. 184-188°C. Anal. Found: C, 46.18; H, 3.33; N, 9.74. Calc. for $C_{32}H_{24}N_6O_3ICu.2H_2O.CH_2Cl_2$: C, 46.52; H, 3.55; N, 9.86.

With cobalt(II) bromide

A solution of cobalt(II) bromide (22.0mg, 0.1mmol) dissolved in acetone (3ml) was layered upon a solution of ligand **4.16** (17.0mg, 0.031mmol) dissolved in chloroform (3ml). A small amount of precipitate appeared at the boundary between the two solutions. A few weeks later the blue precipitate was filtered off. Yield 15.5mg (48%). M.p. 242-245°C. Anal. Found: C, 37.30; H, 3.41; N, 7.80. Calc. for $C_{32}H_{24}N_6O_3Br_4Co_2.3H_2O$: C, 37.24; H, 2.93; N, 8.14 revealing a M_2L complex.

With silver hexafluorophosphate

Ligand **4.16** (21.4mg, 0.039mmol) was dissolved in chloroform (2ml) and overlaid with a solution of silver hexafluorophosphate (10.0mg, 0.039mmol) in acetone. Slow evaporation and vapour diffusion of ether into the mixture gave a fine white precipitate. A few weeks later this white precipitate was filtered off. Yield 22.3mg (10.5%). M.p. 160-162°C. Anal. Found: C, 47.56; H, 3.46; N, 9.35. Calc. for $C_{192}H_{144}N_{36}O_{18}P_7F_{42}Ag_7.8(CH_3)_2CO$: C, 47.36; H, 3.53; N, 9.21 revealing a M_7L_6 complex.

With silver perchlorate

Ligand **4.16** (21.7mg, 0.04mmol) was dissolved in chloroform (2ml) and the silver perchlorate (8.0mg, 0.038mmol) was dissolved in a solution of acetone (3ml). The solutions were mixed together, and left to slowly evaporate with vapor diffusion of ether into the mixture. A fine white precipitate formed overnight, which was collected by filtration and dried *in vacuo*. Yield 32.2mg (79.9%). M.p. 177-180°C. Anal. Found: C, 41.16; H, 3.18; N, 8.16. Calc. for $C_{32}H_{24}N_6O_{11}Cl_2Ag_2.(CH_3)_2CO$: C, 41.49; H, 2.98; N, 8.29 revealing a M_2L complex.

With silver trifluoromethanesulfonate

Ligand **4.16** (19.6mg, 0.036mmol) was dissolved in chloroform (2ml) and layered upon a solution of silver trifluoromethanesulfonate (9.3mg, 0.036mmol) dissolved in acetone (2ml). Ether was diffused into the reaction mixture and slow evaporation gave a white precipitate, which was collected by filtration and dried *in vacuo*. Yield 19.3mg (55.1%). M.p. 125-127°C. Anal. Found: C, 45.57; H, 3.21; N, 8.96. Calc. for

$C_{33}H_{24}N_6O_6F_3SAg.CHCl_3.(CH_3)_2CO$: C, 45.58; H, 3.20; N, 8.62 revealing a 1:1 complex.

Complexes with 4.17

With silver perchlorate

A solution of ligand **4.17** (17.7mg, 0.026mmol) in chloroform (3ml) was layered upon a solution of silver perchlorate (17.3mg, 0.083mmol) dissolved in acetone (2ml). Immediately a white precipitate formed which was collected by filtration and dried *in vacuo*. Yield 13.1mg (24%). M.p. 238-240°C. Anal. Found: C, 53.18; H, 3.73; N, 3.90. Calc. for $C_{94}H_{66}N_6O_{18}Cl_3Ag_3.7H_2O$: C, 53.16; H, 3.80; N, 3.96 revealing a M_3L_2 complex.

With silver trifluoromethanesulfonate

A solution of ligand **4.17** (22.6mg, 0.033mmol) in chloroform (3ml) was layered upon a solution of silver trifluoromethanesulfonate (8.4mg, 0.033mmol) dissolved in acetone (2ml). Slow evaporation of the resulting colourless solution and vapour diffusion of ether gave a white precipitate on standing for a couple of days. The white precipitate was collected by filtration and dried *in vacuo*. Yield 17.6mg (24.7%). M.p. 183-185°C. Anal. Found: C, 53.51; H, 3.54; N, 3.86. Calc. for $C_{97}H_{66}N_6O_{15}F_9S_3Ag_3.H_2O$: C, 53.83; H, 3.17; N, 3.88 revealing a M_3L_2 complex.

With silver tetrafluoroborate

A solution of ligand **4.17** (22.7mg, 0.033mmol) in chloroform (3ml) was layered upon a solution of silver tetrafluoroborate (20.3mg, 0.010mmol) dissolved in acetone (2ml). Immediately a colourless crystalline precipitate formed which was collected by filtration and dried *in vacuo*. Yield 20.4mg (54.5%). M.p. 258-260°C. Anal. Found: C, 52.90; H, 3.78; N, 3.83. Calc. for $C_{47}H_{33}N_3O_3B_2F_8Ag_2.(CH_3)_2CO$: C, 52.90; H, 3.46; N, 3.70 revealing a M_2L complex.

Complexes with 4.18

With silver hexafluorophosphate

A solution of ligand **4.18** (16.5mg, 0.024mmol) in chloroform (3ml) was layered upon a solution of silver hexafluorophosphate (6.0mg, 0.024mmol) dissolved in acetone (2ml). Immediately a white precipitate began to form at the boundary between the two solutions, which was collected a few weeks later by filtration and dried *in vacuo*. Yield 21.3mg (65%). M.p. 178-180°C. Anal. Found: C, 46.86; H, 3.36; N, 6.57. Calc. for $C_{44}H_{30}N_6O_3P_2F_{12}Ag_2.2(CH_3)_2CO$: C, 46.44; H, 3.53; N, 6.13 revealing a M_2L complex.

With silver trifluoromethanesulfonate

A solution of ligand **4.18** (11.6mg, 0.017mmol) in chloroform (3ml) was layered upon a solution of silver trifluoromethanesulfonate (13.2mg, 0.051mmol) dissolved in acetone (2ml). Immediately a white precipitate formed which was collected by filtration and dried *in vacuo*. Yield 5mg (22%). M.p. 180°C. Anal. Found: C, 41.51; H, 2.91; N, 6.12. Calc. for $C_{46}H_{30}N_6O_9F_6S_2Ag_2.CHCl_3.2H_2O$: C, 41.51; H, 2.59; N, 6.18 revealing a M_2L complex.

Complexes with 4.24

With copper(II) chloride

A solution of copper(II) chloride (25.5mg, 0.15mmol) dissolved in methanol (10ml) was layered upon a solution of ligand **4.24** (26.5mg, 0.05mmol) dissolved in hot methanol (10ml). A pale green precipitate formed within minutes, which was collected by filtration. Yield 17.8mg (40.8%). M.p. 264-266°C. Anal. Found: C, 52.09; H, 4.45; N, 4.81. Calc. for $C_{38}H_{33}N_3O_3Cl_4Cu_2.1½H_2O$: C, 52.12; H, 4.14; N, 4.80 revealing a M_2L complex.

With copper(I) iodide

Copper(I) iodide (28.6mg, 0.15mmol) and ligand **4.24** (26.1mg, 0.5mmol) were both dissolved in hot acetonitrile (10ml) and the solutions combined. Immediately a yellow precipitate formed which was collected by filtration and dried *in vacuo*. Yield 27.3mg

(47%). M.p. 258-262°C. Anal. Found: C, 39.34; H, 3.42; N, 3.62. Calc. for $C_{38}H_{33}N_3O_3I_3Cu_3.¾H_2O$: C, 39.19; H, 2.99; N, 3.61 revealing a M_3L complex.

With copper perchlorate

Copper perchlorate (60mg, 0.162mmol) dissolved in methanol (5ml) and added to a solution of ligand **4.24** (30.1mg, 0.051mmol) dissolved in dichloromethane (5ml). A small amount of precipitate appeared at the boundary between the two solutions. A few weeks later the blue precipitate was filtered off. Yield 40.4mg (55%). Anal. Found: C, 32.33; H, 3.62; N, 2.92. Calc. for $C_{38}H_{33}N_3O_{27}Cl_6Cu_3.3H_2O$: C, 32.12; H, 2.77; N, 2.96 revealing a M_3L complex.

With silver hexafluorophosphate

A solution of ligand **4.24** (22.6mg, 0.038mmol) in chloroform (3ml) was layered upon a solution of silver hexafluorophosphate (9.8mg, 0.038mmol) dissolved in acetone (2ml). Immediately a white precipitate formed which was collected by filtration and dried *in vacuo*. Yield 22.7mg (70.2%). M.p. 181-182°C. Anal. Found: C, 54.74; H, 4.59; N, 4.98. Calc. for $C_{38}H_{33}N_3O_3PF_6Ag.⅓(CH_3)_2CO$: C, 54.99; H, 4.14; N, 4.93 revealing a 1:1 complex.

With zinc bromide

Ligand **4.24** (27.6mg, 0.05mmol) and zinc bromide (33.7mg, 0.15mmol) were both dissolved in hot methanol and the solutions were combined and left to cool. A white precipitate formed immediately, which was collected by filtration a few weeks later. Yield 30.6mg (47.1%). M.p. 169-173°C. Anal. Found: C, 34.97; H, 3.24; N, 3.20. Calc. for $C_{38}H_{33}N_3O_3Br_6Zn_3.3H_2O$: C, 34.86; H, 3.00; N, 3.21 revealing a M_3L complex.

Complexes with 4.25

With copper(II) chloride

A solution of copper(II) chloride (15.3mg, 0.09mmol) dissolved in methanol (10ml) was layered upon a solution of ligand **4.25** (19.6mg, 0.03mmol) dissolved in dichloromethane (10ml). Immediately a green precipitate formed at the boundary

between the two solutions. A few weeks later this pale green precipitate was filtered off. Yield 24.3mg (81%). M.p. 183-190°C. Anal. Found: C, 46.62; H, 4.01; N, 4.16. Calc. for $C_{38}H_{33}N_3O_3Cl_6Cu_3.⅔CH_3OH$: C, 46.24; H, 3.58; N, 4.18 revealing a M_3L complex.

With copper(I) iodide

Copper(I) iodide (28.6mg, 0.15mmol) and ligand **4.25** (26.6mg, 0.05mmol) were both dissolved in hot acetonitrile (10ml) and combined. Immediately a yellow precipitate formed which was collected by filtration and dried *in vacuo*. Yield 29.1mg (18.4%). M.p. 229-230°C. Anal. Found: C, 43.28; H, 3.41; N, 3.89. Calc. for $C_{114}H_{99}N_9O_9I_7Cu_7.5H_2O$: C, 43.30; H, 3.47; N, 3.99 revealing a M_7L_3 complex.

With silver trifluoromethanesulfonate

A solution of ligand **4.25** (25.1mg, 0.043mmol) in acetone (3ml) was layered upon a solution of silver trifluoromethanesulfonate (11.1mg, 0.043mmol) dissolved in acetone (2ml). Immediately a white precipitate formed which was collected by filtration a few weeks later and dried *in vacuo*. Yield 29.8mg (81.2%). M.p. 139-141°C. Anal. Found: C, 54.91; H, 4.19; N, 4.84. Calc. for $C_{39}H_{33}N_3O_6F_3SAg.H_2O$: C, 54.81; H, 4.13; N, 4.92 revealing a 1:1 complex.

With zinc bromide

Ligand **4.25** (22.5mg, 0.04mmol) and zinc bromide (27.0mg, 0.12mmol) were both dissolved in hot methanol and the solutions were combined and left to cool. A white precipitate formed immediately, which was collected by filtration a few weeks later. Yield 29.5mg (39.3%). M.p. 199-208°C. Anal. Found: C, 48.34; H, 3.79; N, 4.43. Calc. for $C_{38}H_{33}N_3O_3Br_6Zn_3.3H_2O$: C, 48.32; H, 3.84; N, 4.45 revealing a M_3L_2 complex.

Complexes with 4.26

With cobalt(II) bromide

A solution of cobalt(II) bromide (33.6mg, 0.154mmol) dissolved in acetone (3ml) was layered upon a solution of ligand **4.26** (28.9mg, 0.05mmol) also dissolved in acetone (3ml). A precipitate formed immediately on mixing. A few weeks later the purple

precipitate was collected by filtration and dried *in vacuo*. Yield 24.4mg (26.3%). M.p. 277-279°C. Anal. Found: C, 48.63; H, 4.13; N, 4.42. Calc. for $C_{76}H_{66}N_6O_6Br_6Co_3.3H_2O$: C, 48.82; H, 3.88; N, 4.49 revealing a M_3L_2 complex.

With copper(I) iodide

Copper(I) iodide (28.9mg, 0.15mmol) and ligand **4.26** (29.4mg, 0.05mmol) were both dissolved in hot acetonitrile (5ml) and combined. Immediately a yellow precipitate formed which was collected by filtration and dried *in vacuo*. Yield 18.8mg (33%). M.p. 182-184°C. Anal. Found: C, 40.76; H, 3.42; N, 3.83. Calc. for $C_{38}H_{33}N_3O_3Cl_8Cu_4$: C, 40.84; H, 2.98; N, 3.76 revealing a M_4L complex.

With silver perchlorate

A solution of ligand **4.26** (23.6mg, 0.041mmol) in chloroform (3ml) was layered upon a solution of silver perchlorate (24.5mg, 0.12mmol) dissolved in acetone (2ml). Immediately a white precipitate formed which was collected by filtration and dried *in vacuo*. Yield 20.4mg (27%). M.p. 150°C. Anal. Found: C, 48.92; H, 4.25; N, 4.47. Calc. for $C_{76}H_{66}N_6O_{18}Cl_3Ag_3.5H_2O$: C, 48.78; H, 4.09; N, 4.49 revealing a M_3L_2 complex.

Preparation of complexes with the 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5'6,6'-tetrol ligands

Complexes with 4.33

With cobalt(II) bromide

A solution of cobalt(II) bromide (33.0mg, 0.15mmol) dissolved in acetone (3ml) was layered upon a solution of ligand **4.33** (24.1mg, 0.037mmol) dissolved in hot acetone (3ml). The solution was concentrated down by slow evaporation to give a blue crystalline solid that was collected by filtration and dried *in vacuo*. Yield 41.4mg (95.5%). M.p. 304-307°C. Anal. Found: C, 42.04; H, 3.69; N, 4.51. Calc. for $C_{41}H_{36}N_4O_4Br_4Co_2.5H_2O$: C, 41.86; H, 3.94; N, 4.76 revealing a M_2L complex.

With cobalt(II) chloride

A solution of cobalt(II) chloride (34.6mg, 0.148mmol) dissolved in acetone (3ml) was layered upon a solution of ligand **4.33** (24.1mg, 0.037mmol) dissolved in a hot acetone solution (3ml). The solution was concentrated down by slow evaporation to give a blue crystalline solid that was collected by filtration and dried *in vacuo*. Yield 29.9mg (70.5%). M.p. 281-284°C. Anal. Found: C, 45.62; H, 4.37; N, 4.91. Calc. for $C_{41}H_{36}N_4O_4Cl_6Co_3.3H_2O.(CH_3)_2CO$: C, 45.94; H, 4.21; N, 4.87 revealing a M_3L complex.

With copper(II) chloride

A solution of copper(II) chloride (25.6mg, 0.15mmol) was dissolved in methanol (5ml) was layered upon a solution of ligand **4.33** (24.5mg, 0.037mmol) dissolved in dichloromethane (5ml). On standing for a few weeks a green solid precipitated out which was collected and dried *in vacuo*. Yield 39.5mg (92.4%). M.p. 220-223°C. Anal. Found: C, 42.53; H, 4.03; N, 4,73. Calc. for $C_{41}H_{36}N_4O_4Cl_6Cu_3.6H_2O$: C, 42.44; H, 4.17; N, 4.83 revealing a M_3L complex.

With copper nitrate

A solution of copper nitrate (40.5mg, 0.167mmol) dissolved in methanol (5ml) was added to a solution of ligand **4.33** (26.5mg, 0.041mmol) dissolved in dichloromethane (5ml). The solution was concentrated by slow evaporation to give a sky blue crystalline solid that was filtered off. Yield 38mg (63.1%). M.p. 227-228°C. Anal. Found: C, 33.63; H, 3.40; N, 11.05. Calc. for $C_{41}H_{36}N_{12}O_{28}Cu_4.4H_2O$: C, 33.48; H, 3.01; N, 11.43 revealing a M_4L complex.

With copper(II) perchlorate

Copper(II) perchlorate (62.8mg, 0.169mmol) dissolved in acetone (5ml) and added to a solution of ligand **4.33** (27.6mg, 0.042mmol) dissolved in hot acetone (5ml). After a few minutes the solution went cloudy and a blue precipitate began to form. A few weeks later the sky blue precipitate was filtered off. Yield 73.3mg (93.2%). M.p. 160°C. Anal. Found: C, 26.60; H, 3.51; N, 2.80. Calc. for $C_{41}H_{36}N_4O_{36}Cl_8Cu_4.10H_2O$: C, 26.21; H, 3.00; N, 2.98 revealing a M_4L complex.

With palladium chloride

Palladium chloride (35.6mg, 0.2mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **4.33** (30.9mg, 0.05mmol). Immediately the solution went cloudy and a yellow precipitate began to form. A few weeks later the yellow precipitate was filtered off and dried *in vacuo*. Yield 42.4mg (79.7%). M.p. >350°C. Anal. Found: C, 46.09; H, 3.82; N, 5.22. Calc. for $C_{41}H_{36}N_4O_4Cl_4Pd_2.3½H_2O$: C, 46.18; H, 4.06; N, 5.25 revealing a M_2L complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (64.1mg, 0.167mmol) in acetone (6ml) was layered upon a solution of ligand **4.33** (27.7mg, 0.042mmol) dissolved in hot acetone (5ml). Immediately an orange precipitate formed which was collected and dried *in vacuo*. Yield 20.7mg (40.1%). M.p. >350°C. Anal. Found: C, 39.86; H, 3.18; N, 4.28. Calc. for $C_{41}H_{36}N_4O_4Cl_3Pd_3.3H_2O$: C, 39.88; H, 3.43; N, 4.54 revealing a M_3L complex.

With zinc bromide

Zinc bromide (36.0mg, 0.16mmol) was dissolved in methanol (5ml) and layered upon a solution of ligand **4.33** (26.0mg, 0.04mmol) dissolved in dichloromethane (5ml) to give a colourless solution. A crystalline solid appeared on standing for a few weeks. Yield 34.8mg (62.8%). M.p. 275-276°C. Anal. Found: C, 35.21; H, 3.35; N, 3.89. Calc. for $C_{41}H_{36}N_4O_4Br_6Zn_3.4H_2O$: C, 35.26; H, 3.18; N, 4.01 revealing a M_3L complex.

With zinc chloride

Zinc chloride (22.0mg, 0.16mmol) was dissolved in methanol (5ml) and layered upon a solution of ligand **4.33** (25.4mg, 0.04mmol) dissolved in dichloromethane (5ml) to give a colourless solution. Slow evaporation of the reaction mixture formed a residue which was recrystallised from an acetone:methanol solution. A colourless crystalline solid appeared on standing for a few weeks. Yield 27.7mg (54.4%). M.p. 254-255°C. Anal. Found: C, 42.03; H, 3.87; N, 4.71. Calc. for $C_{41}H_{36}N_4O_4Cl_8Zn_4.CH_3OH.(CH_3)_2CO$: C, 42.09; H, 3.61; N, 4.36 revealing a M_4L complex.

Complexes with 4.35

With palladium chloride

Palladium chloride (17.2mg, 0.09mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol:dichloromethane solution of ligand **4.35** (19mg, 0.023mmol). Immediately the solution went cloudy and a yellow precipitate began to form. A few weeks later the yellow precipitate was filtered off and dried *in vacuo*. Yield 4.9mg (18.2%). M.p. 299-300°C. Anal. Found: C, 58.32; H, 4.33; N, 4.51. Calc. for $C_{57}H_{44}N_4O_4Cl_2Pd.H_2O.2CH_2Cl_2$: C, 58.36; H, 4.15; N, 4.61 revealing a 1:1 complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (34.9mg, 0.09mmol) in acetone (6ml) was layered upon a solution of ligand **4.35** (19.2mg, 0.023mmol) dissolved in hot acetone (5ml). Immediately an orange precipitate formed which was collected and dried *in vacuo*. Yield 9.2mg (26.2%). M.p. 320°C. Anal. Found: C, 43.57; H, 3.13; N, 3.33. Calc. for $C_{57}H_{44}N_4O_4Cl_8Pd_4$: C, 43.93; H, 2.85; N, 3.60 revealing a M_4L complex.

Complexes with 4.36

With copper(II) chloride

A solution of copper(II) chloride (23.1mg, 0.136mmol) dissolved in methanol (5ml) was layered upon a solution of ligand **4.36** (28.6mg, 0.034mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting pale green solution produced a green precipitate that was collected by filtration and dried *in vacuo*. Yield 40.7mg (77.4%). M.p. 234-235°C. Anal. Found: C, 40.88; H, 3.65; N, 6.93. Calc. for $C_{53}H_{40}N_8O_4Cl_8Cu_4.9H_2O$: C, 40.99; H, 3.76; N, 7.22 revealing a M_4L complex.

With copper(I) iodide

A solution of copper(I) iodide (24.0mg, 0.128mmol) dissolved in acetonitrile (5ml) was carefully layered onto a solution of ligand **4.36** (27.1mg, 0.032mmol) dissolved in dichloromethane (5ml). A brown/orange solid appeared on standing for a few weeks, which was filtered off and dried *in vacuo*. Yield 29.6mg (22.7%). M.p. 295-297°C.

Anal. Found: C, 46.19; H, 3.02; N, 7.89. Calc. for $C_{159}H_{120}N_{24}O_{12}I_8Cu_8$: C, 46.78; H, 2.96; N, 8.23 revealing a M_8L_3 complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (53.9mg, 0.14mmol) in acetone (5ml) was layered upon a solution of ligand **4.36** (29.7mg, 0.035mmol) dissolved in chloroform (5ml). Immediately a yellow precipitate formed at the boundary between the two solutions. A few weeks later the yellow solid was filtered off and dried *in vacuo*. Yield 38.7mg (68.5%). M.p. >340°C. Anal. Found: C, 41.49; H, 2.92; N, 6.79. Calc. for $C_{53}H_{40}N_8O_4Cl_8Pd_4.(CH_3)_2CO$: C, 41.51; H, 2.86; N, 6.92 revealing a M_4L complex.

Complexes with 4.37

With cobalt(II) bromide

A solution of cobalt(II) bromide (37.4mg, 0.17mmol) dissolved in acetone (3ml) was layered upon a solution of ligand **4.37** (30.5mg, 0.04mmol) dissolved in hot acetone (3ml). A dark green/blue solid precipitated immediately from the reaction mixture, which was collected by filtration. Yield 56.9mg (94.8%). M.p. >350°C. Anal. Found: C, 41.44; H, 4.25; N, 3.38. Calc. for $C_{45}H_{44}N_4O_4Br_6Co_3.2½(CH_3)_2CO$: C, 41.86; H, 3.95; N, 3.72 revealing a M_3L complex.

With copper(II) chloride

A solution of copper(II) chloride (30.0mg, 0.176mmol) dissolved in methanol (5ml) was layered upon a solution of ligand **4.37** (31.5mg, 0.044mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting pale green solution produced a dark green precipitate that was recrystallised from acetone:dichloromethane, collected by filtration and dried *in vacuo*. Yield 38.5mg (67%). M.p. 166-167°C. Anal. Found: C, 44.50; H, 4.07; N, 3.88. Calc. for $C_{45}H_{44}N_4O_4Cl_8Cu_4.(CH_3)_2CO.CH_3OH$: C, 44.16; H, 4.08; N, 4.20 revealing a M_4L complex.

With copper(I) iodide

A solution of copper(I) iodide (38.2mg, 0.2mmol) dissolved in acetonitrile (5ml) was carefully layered onto a solution of ligand **4.37** (36.3mg, 0.05mmol) dissolved in dichloromethane (5ml). Immediately a precipitate began to form at the boundary between the two solutions. A few weeks later this brown precipitate was filtered off. Yield 55.7mg (76.1%). M.p. 323-324°C. Anal. Found: C, 36.61; H, 3.01; N, 3.24. Calc. for $C_{45}H_{44}N_4O_4I_4Cu_4$: C, 36.85; H, 3.02; N, 3.82 revealing a M_4L complex.

With copper nitrate

To a hot solution of ligand **4.37** (30.1mg, 0.042mmol) dissolved in hot methanol (5ml) was added a solution of copper nitrate (42.2mg, 0.17mmol) dissolved in methanol (5ml). The resulting solution went grey and cloudy and a precipitate began to form. The precipitate was collected by filtration and dried *in vacuo*. Yield 6.8mg (16.8%). M.p. 200-201°C. Anal. Found: C, 56.10; H, 4.97; N, 8.58. Calc. for $C_{45}H_{44}N_6O_{10}Cu_2.½H_2O$: C, 56.01; H, 4.70; N, 8.71 revealing a M_2L complex.

With palladium chloride

Palladium chloride (40.6mg, 0.23mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **4.37** (39.7mg, 0.056mmol). Immediately the solution went cloudy and a yellow precipitate began to form. A few weeks later the yellow precipitate was filtered off and dried *in vacuo*. Yield 32mg (50.4%). M.p. >340°C. Anal. Found: C, 48.10; H, 4.41; N, 4.49. Calc. for $C_{45}H_{44}N_4O_4Cl_4Pd_2.4H_2O$: C, 47.76; H, 4.63; N, 4.95 revealing a M_2L complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (74.0mg, 0.19mmol) in acetone (6ml) was layered upon a solution of ligand **4.37** (34.0mg, 0.048mmol) dissolved in hot acetone (5ml). Immediately an orange precipitate formed which was collected and dried *in vacuo*. Yield 40.3mg (62.3%). M.p. >350°C. Anal. Found: C, 45.21; H, 3.95; N, 4.37. Calc. for $C_{45}H_{44}N_4O_4Cl_6Pd_3.2(CH_3)_2CO$: C, 45.27; H, 4.17; N, 4.14 revealing a M_3L complex.

With zinc bromide

Ligand **4.37** (28.4mg, 0.04mmol) and zinc bromide (37.0mg, 0.16mmol) were both dissolved in hot methanol and the solutions were combined and left to cool. A white crystalline precipitate formed immediately, which was collected by filtration and washed with 1:1 acetone:methanol. Yield 57.7mg (87.4%). M.p. 261-263°C. Anal. Found: C, 34.88; H, 3.44; N, 3.04. Calc. for $C_{45}H_{44}N_4O_4Br_8Zn_4.(CH_3)_2CO$: C, 34.65; H, 3.03; N, 3.37 revealing a M_4L complex.

Complexes with 4.38

With cobalt(II) chloride

Cobalt(II) chloride (38.4mg, 0.161mmol) was dissolved in acetone (3ml) and layered upon a solution of ligand **4.38** (29.6mg, 0.04mmol) dissolved in hot acetone (3ml). A dark blue solid precipitated immediately from the reaction mixture, which was collected by filtration. Yield 17.2mg (33.6%). M.p. 202-205°C. Anal. Found: C, 42.47; H, 4.32; N, 3.99. Calc. for $C_{45}H_{44}N_4O_4Cl_8Co_4.3¼H_2O$: C, 42.13; H, 3.97; N, 4.37 revealing a M_4L complex.

With copper(II) chloride

A solution of copper(II) chloride (28.6mg, 0.168mmol) dissolved in methanol (5ml) was carefully layered upon a solution of ligand **4.38** (30.0mg, 0.042mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting pale green solution produced a brown/green precipitate that was collected by filtration and dried *in vacuo*. Yield 42.6mg (76.5%). M.p. 218-220°C. Anal. Found: C, 40.28; H, 4.15; N, 3.84. Calc. for $C_{45}H_{44}N_4O_4Cl_8Cu_4.5H_2O$: C, 40.55; H, 4.08; N, 4.20 revealing a Cu_4L complex.

With copper(I) iodide

A solution of copper(I) iodide (42.6mg, 0.22mmol) dissolved in acetonitrile (5ml) was carefully layered onto a solution of ligand **4.38** (39.5mg, 0.056mmol) dissolved in hot acetonitrile (5ml). A yellow precipitate formed immediately, which was collected by filtration. Yield 50.1mg (32%). M.p. 205-206°C. Anal. Found: C, 38.40; H, 3.25; N,

3.70. Calc. for $C_{90}H_{88}N_8O_8I_7Cu_7.3H_2O$: C, 38.65; H, 3.39; N, 4.01 revealing a M_7L_2 complex.

With copper nitrate

To a hot solution of ligand **4.38** (33.0mg, 0.05mmol) dissolved in methanol (5ml), was added a solution of copper nitrate (49.4mg, 0.2mmol) in methanol (5ml). The resulting solution went grey and cloudy and a precipitate began to form. The purple/grey solid was collected by filtration and dried *in vacuo*. Yield 16.5mg (36.3%). M.p. 170-172°C. Anal. Found: C, 59.07; H, 5.18; N, 9.07. Calc. for $C_{45}H_{44}N_6O_{10}Cu.H_2O$: C, 59.37; H, 5.09; N, 9.23 revealing a 1:1 complex.

With palladium chloride

Palladium chloride (40.9mg, 0.23mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **4.38** (40.0mg, 0.057mmol). Immediately the solution went cloudy and a yellow precipitate began to form. A few weeks later the yellow precipitate was filtered off and dried *in vacuo*. Yield 39.7mg (62.1%). M.p. >350°C. Anal. Found: C, 47.83; H, 4.42; N, 4.69. Calc. for $C_{45}H_{44}N_4O_4Cl_4Pd_2.4H_2O$: C, 47.76; H, 4.63; N, 4.95 revealing M_2L complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (72.4mg, 0.19mmol) in acetone (6ml) was layered upon a solution of ligand **4.38** (33.4mg, 0.047mmol) dissolved in hot acetone (5ml). Immediately an orange precipitate formed which was collected and dried *in vacuo*. Yield 47.8mg (86.6%). M.p. >350°C. Anal. Found: C, 46.78; H, 3.86; N, 4.93. Calc. for $C_{45}H_{44}N_4O_4Cl_4Pd_2.CHCl_3$: C, 46.87; H, 3.85; N, 4.75 revealing M_2L complex.

With zinc chloride

Ligand **4.38** (34.4mg, 0.05mmol) and zinc chloride (28.8mg, 0.21mmol) were both dissolved in hot methanol and the solutions were combined and left to cool. A white crystalline precipitate formed immediately at the boundary between the two solutions. A few weeks later a white crystalline precipitate was filtered off and dried *in vacuo*. Yield 18.6mg (38.3%). M.p. 217-219°C. Anal. Found: C, 55.25; H, 4.78; N, 5.57. Calc. for $C_{45}H_{44}N_4O_4Cl_4Zn_2$: C, 55.30; H, 4.54; N, 5.73 revealing M_2L complex.

Preparation of complexes with the Bisphenol P ligands

Complexes with 5.10

With cobalt(II) bromide, viz **5.14**

Cobalt(II) bromide (27.9mg, 0.127mmol) was dissolved in acetone (3ml) and layered upon a solution of ligand **5.10** (33.0mg, 0.066mmol) dissolved in an acetone: dichloromethane solution (3ml). Slow evaporation of the resulting blue solution over two days produced beautiful blue block-like crystals of **5.14** suitable for X-ray crystallography. X-ray analysis revealed a 1-dimensional coordination polymer. Yield 30.7mg (52%). M.p. 202-204°C. Anal. Found: C, 50.82; H, 4.72; N, 3.06. Calc. for $C_{34}H_{32}N_2O_2Br_2Co.CH_2Cl_2.(CH_3)_2CO.2H_2O$: C, 50.80; H, 4.94; N, 3.12.

With cobalt(II) chloride, viz **5.15**

A solution of cobalt(II) chloride (33.0mg, 0.138mmol) dissolved in acetone (3ml) was layered upon a solution of ligand **5.10** (32.7mg, 0.065mmol) dissolved in a hot acetone: dichloromethane solution (3ml). Slow evaporation of the resulting blue solution over a period of four days produced clusters of blue star-like crystals of **5.15** suitable for X-ray crystallography. Yield 36.1mg (63.6%). M.p. 273-276°C. Anal. Found: C, 53.48; H, 4.71; N, 3.60. Calc. for $C_{34}H_{32}N_2O_2Cl_2Co.2CH_2Cl_2.(CH_3)_2CO.H_2O$: C, 53.45; H, 5.06; N, 3.20.

With copper chloride

A solution of copper chloride (29.6mg, 0.17mmol) dissolved in methanol (5ml) and layered upon a solution of ligand **5.10** (43.1mg, 0.086mmol) dissolved in hot methanol (5ml). The solution turned pale green and a fine green precipitate formed on standing. This was collected by filtration and dried *in vacuo*. Yield 31mg (46.5%). M.p. 233-237°C. Anal. Found: C, 53.28; H, 4.85; N, 3.44. Calc. for $C_{34}H_{32}N_2O_2Cl_4Cu_2.¼CH_3OH$: C, 52.91; H, 4.28; N, 3.60 revealing a M_2L complex.

With copper perchlorate

Copper perchlorate (49.5mg, 0.134mmol) dissolved in methanol (5ml) and added to a solution of ligand **5.10** (33.6mg, 0.067mmol) dissolved in dichloromethane (5ml). Slow

evaporation produced a blue solid. Yield 26.9mg (31.8%). M.p. 277°C. Anal. Found: C, 64.28; H, 5.24; N, 4.32. Calc. for $C_{68}H_{64}N_4O_{12}Cl_2Cu$: C, 64.63; H, 5.10; N, 4.43 revealing a ML_2 complex.

With palladium chloride

Palladium chloride (25.0mg, 0.146mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **5.10** (36.4mg, 0.073mmol). Immediately the solution went cloudy and a yellow precipitate began to form. A few weeks later the yellow precipitate was filtered off, washed with methanol and dried *in vacuo*. Yield 22.9mg (45.8%). M.p. 276°C. Anal. Found: C, 59.76; H, 4.80; N, 3.96. Calc. for $C_{34}H_{32}N_2O_2Cl_2Pd.½H_2O$: C, 59.44; H, 4.84; N, 4.08 revealing a 1:1 complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (58.3mg, 0.152mmol) in acetone (6ml) was layered upon a solution of ligand **5.10** (37.4mg, 0.075mmol) dissolved in hot acetone (5ml). Immediately a yellow precipitate formed which was collected and dried *in vacuo*. Yield 10.5mg (17.5%). M.p. 274-275°C. Anal. Found: C, 50.90; H, 4.23; N, 3.31. Calc. for $C_{34}H_{32}N_2O_2Cl_2Pd_2.H_2O$: C, 50.89; H, 4.27; N, 3.49 revealing a M_2L complex.

Complexes with 5.11

With copper(II) chloride, viz **5.16**

A solution of copper(II) chloride (18.5mg, 0.10mmol) dissolved in methanol (5ml) was layered upon a solution of ligand **5.11** (27.2mg, 0.054mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting solution produced green crystalline plates of **5.16** suitable for X-ray crystallography. The X-ray analysis revealed an intriguing structure consisting of three ligand strands linked by Cu_3Cl_6 bridging motifs. Yield 27.3mg (26.5%). M.p. 254-256°C. Anal. Found: C, 45.24; H, 4.58; N, 5.86. Calc. for $C_{96}H_{90}N_{12}O_6Cl_6Cu_2.6H_2O.9CH_2Cl_2$: C, 45.30; H, 4.35; N, 6.04.

With copper perchlorate

Copper perchlorate (40.0mg, 0.108mmol) and ligand **5.11** (27.3mg, 0.054mmol) were both dissolved in hot acetone, allowed to cool and combined. After a few weeks a green crystalline solid formed. This was collected, washed with acetone and dried *in vacuo*. Yield 22.8mg (39%). Anal. Found: C, 39.16; H, 3.37; N, 5.39. Calc. for $C_{32}H_{30}N_4O_{18}Cl_4Cu_2.1½(CH_3)_2CO$: C, 39.33; H, 3.53; N, 5.03 revealing a M_2L complex.

With palladium chloride

Palladium chloride (19.0mg, 0.107mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **5.11** (26.0mg, 0.052mmol). Immediately the solution went cloudy and a yellow precipitate began to form. A few weeks later the yellow precipitate was filtered off, washed with methanol and dried *in vacuo*. Yield 23.2mg (33.7%). M.p. 218-219°C. Anal. Found: C, 58.06; H, 4.69; N, 8.42. Calc. for $C_{32}H_{30}N_4O_2ClPd.2H_2O$: C, 58.01; H, 4.87; N, 8.46 revealing a ML complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (39.8mg, 0.104mmol) in acetone (6ml) was layered upon a solution of ligand **5.11** (26.4mg, 0.052mmol) dissolved in hot acetone (5ml). Immediately an orange precipitate formed which was collected, washed with acetone and dried *in vacuo*. Yield 30.9mg (67.4%). M.p. 284-285°C. Anal. Found: C, 45.27; H, 3.66; N, 6.31. Calc. for $C_{32}H_{30}N_4O_2Cl_4Pd_2.½(CH_3)_2CO$: C, 45.40; H, 3.75; N, 6.32 revealing a M_2L complex.

Complexes with 5.12

With copper(II) chloride

A solution of copper(II) chloride (17.0mg, 0.1mmol) dissolved in methanol (5ml) was layered upon a solution of ligand **5.12** (29.0mg, 0.05mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting pale green solution produced a khaki solid that was collected by filtration. Yield 38.8mg (38.9%). M.p. 281-283°C. Anal. Found: C, 50.35; H, 4.42; N, 2.76. Calc. for $C_{84}H_{72}N_4O_4Cl_{10}Cu_5.7H_2O$: C, 50.45; H, 4.33; N, 2.80 revealing a M_5L_2 complex.

With palladium chloride

Palladium chloride (16.6mg, 0.094mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot 1:1 methanol:dichloromethane solution of ligand **5.12** (28.2mg, 0.047mmol). A yellow crystalline precipitate formed after three weeks, which was filtered off and dried *in vacuo*. Yield 13.7mg (37.6%). M.p. 322-324°C. Anal. Found: C, 64.58; H, 4.90; N, 3.56. Calc. for $C_{42}H_{36}N_2O_2Cl_2Pd$: C, 64.83; H, 4.66; N, 3.60 revealing a 1:1 complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (33.7mg, 0.087mmol) in acetone (5ml) was layered upon a solution of ligand **5.12** (26.1mg, 0.043mmol) dissolved in chloroform (5ml). Immediately a yellow precipitate formed at the boundary between the two solutions. A few weeks later the yellow solid was filtered off and dried *in vacuo*. Yield 23.3mg (61.3%). M.p. 306°C. Anal. Found: C, 56.94; H, 4.26; N, 3.31. Calc. for $C_{42}H_{36}N_2O_2Cl_2Pd.6H_2O$: C, 56.93; H, 5.46; N, 3.16 revealing a 1:1 complex.

Complexes with 5.13

With copper(I) iodide

A solution of copper(I) iodide (12.6mg, 0.068mmol) dissolved in acetonitrile (5ml) was carefully layered upon a solution of ligand **5.13** (20.5mg, 0.034mmol) dissolved in dichloromethane (5ml) to give a yellow solution. A yellow crystalline precipitate appeared on standing for a few weeks, which was filtered off and dried *in vacuo*. Yield 8.4mg (6.2%). M.p. 180°C. Anal. Found: C, 72.47; H, 45.14; N, 8.80. Calc. for $C_{120}H_{102}N_{12}O_6ICu$: C, 72.11; H, 5.14; N, 8.41 revealing a ML_3 complex.

With palladium chloride

Palladium chloride (15.2mg, 0.086mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol: dichloromethane solution of ligand **5.13** (25mg, 0.042mmol). A small amount of yellow precipitate appeared at the boundary between the two solutions. A few weeks later the yellow precipitate was filtered off and dried *in vacuo*. Yield 23.6mg (37.5%). M.p. 286-288°C. Anal. Found: C, 64.83; H, 4.81; N, 7.28. Calc.

for $C_{80}H_{68}N_8O_4Cl_2Pd.2H_2O.CH_2Cl_2$: C, 64.70; H, 4.96; N, 7.45 revealing a ML_2 complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (35.4mg, 0.093mmol) in acetone (5ml) was layered upon a solution of ligand **5.13** (27.3mg, 0.045mmol) dissolved in chloroform (5ml). Immediately a yellow precipitate formed at the boundary between the two solutions. A few weeks later the yellow solid was filtered off and dried *in vacuo*. Yield 28.3mg (62%). M.p. 280-284°C. Anal. Found: C, 50.97; H, 3.92; N, 5.62. Calc. for $C_{40}H_{34}N_4O_2Cl_4Pd_2.(CH_3)_2CO$: C, 50.86; H, 3.97; N, 5.52 revealing a M_2L complex.

Complexes with 5.17

With cobalt(II) bromide

A solution of cobalt(II) bromide (19.3mg, 0.091mmol) dissolved in acetone (3ml) was layered upon a solution of ligand **5.17** (24.1mg, 0.045mmol) dissolved in a 1:1 acetone:chloroform (3ml) solution. The solution was concentrated by slow evaporation to give a blue precipitate that was collected by filtration and dried *in vacuo*. Yield 28.4mg (27.6%). M.p. 298-300°C. Anal. Found: C, 56.36; H, 4.97; N, 3.58. Calc. for $C_{36}H_{36}N_2O_2Br_2Co.H_2O$: C, 56.49; H, 5.00; N, 3.66 revealing a ML complex.

With cobalt(II) chloride

A solution of cobalt(II) chloride (19.0mg, 0.08mmol) dissolved in hot acetone (3ml) was layered upon a solution of ligand **5.17** (21.1mg, 0.04mmol) dissolved in a 1:1 acetone:chloroform (3ml) solution. The resulting blue solution was concentrated by slow evaporation to give a blue precipitate that was collected by filtration and dried *in vacuo*. Yield 27.2mg (84.5%). M.p. 310-312°C. Anal. Found: C, 53.94; H, 5.07; N, 3.45. Calc. for $C_{36}H_{36}N_2O_2Cl_4Co_2.H_2O$: C, 53.62; H, 4.75; N, 3.47 revealing a M_2L complex.

With copper nitrate

A solution of copper nitrate (20.0mg, 0.08mmol) dissolved in methanol (5ml) was layered upon a solution of ligand **5.17** (22.0mg, 0.04mmol) in methanol (5ml). The solution was concentrated by slow evaporation to give a beautiful blue crystalline solid that was collected by filtration and dried *in vacuo*. These crystals were found to be stacks of very fine plate-like crystals that were not suitable for X-ray crystallography, despite several attempts. Yield 10.6mg (21.3%). M.p. 145-149°C. Anal. Found: C, 69.25; H, 5.86; N, 6.70. Calc. for $C_{72}H_{72}N_6O_{10}Cu$: C, 69.46; H, 5.83; N, 6.75 revealing a ML_2 complex

With copper perchlorate

Copper perchlorate (37.0mg, 0.1mmol) dissolved in methanol (5ml) and added to a solution of ligand **5.17** (26.0mg, 0.049mmol) dissolved in dichloromethane (5ml). Slow evaporation produced a blue solid. Yield 25.4mg (38.4%). M.p. 197-199°C. Anal. Found: C, 64.52; H, 5.77; N, 4.09. Calc. for $C_{72}H_{72}N_4O_{12}Cl_2Cu.CH_3OH$: C, 64.86; H, 5.67; N, 4.14 revealing a ML_2 complex.

With palladium chloride

Palladium chloride (18.0mg, 0.102mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **5.17** (26.3mg, 0.05mmol). Immediately the solution went cloudy and a orange precipitate began to form. A few weeks later the peach precipitate was filtered off, washed with methanol and dried *in vacuo*. Yield 15.7mg (40.9%). M.p. 332-324°C. Anal. Found: C, 55.79; H, 5.11; N, 3.46. Calc. for $C_{36}H_{36}N_2O_2Cl_2Pd.3½H_2O$: C, 56.22; H, 5.64; N, 3.64 revealing a 1:1 complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (37mg, 0.096mmol) in acetone (5ml) was layered upon a solution of ligand **5.17** (25.6mg, 0.048mmol) dissolved in chloroform (5ml). Immediately a yellow precipitate formed at the boundary between the two solutions. The yellow precipitate was dissolved in acetonitrile and after a month the yellow crystalline was filtered off and dried *in vacuo*. Yield 17.9mg (46.4%). M.p. 308-311°C. Anal. Found: C, 57.11; H, 4.64; N, 5.16. Calc. for $C_{36}H_{36}N_2O_2Cl_2Pd.CH_3CN.½CHCl_3$: C, 57.32; H, 4.94; N, 5.21 revealing a 1:1 complex.

Complexes with 5.18

With silver hexafluorophosphate, viz **5.20**

Ligand **5.18** (25mg, 0.047mmol) was dissolved in chloroform (2ml) and layered upon a solution of silver hexafluorophosphate (14.0mg, 0.055mmol) dissolved in acetone (2ml). Slow evaporation and vapour diffusion of ethyl ether into the reaction mixture gave a white precipitate at the bottom of the vial and chunks of block-like colourless crystals of **5.20** on the sides of the vial suitable for X-ray crystallography which revealed a 1:1 complex. Yield 27.6mg (67.3%). M.p. 238-239°C. Anal. Found: C, 54.65; H, 5.05 N, 3.48. Calc. for $C_{36}H_{36}N_2O_2PF_6Ag.2CH_3CH_2OH$: C, 54.99; H, 5.54; N, 3.21.

With cobalt(II) bromide

A solution of cobalt(II) bromide (19.3mg, 0.088mmol) dissolved in acetone (3ml) was layered upon a solution of ligand **5.18** (22.2mg, 0.042mmol) also dissolved in hot acetone (3ml). The solution was concentrated by slow evaporation to give a blue crystalline solid that was collected by filtration and dried *in vacuo*. Yield 13.7mg (39.9%). M.p. 288-289°C. Anal. Found: C, 53.06; H, 5.12; N, 3.36. Calc. for $C_{36}H_{36}N_2O_2Br_2Co.4H_2O$: C, 52.76; H, 5.41; N, 3.42 revealing a 1:1 complex.

With cobalt(II) chloride

A solution of cobalt(II) chloride (20.4mg, 0.085mmol) dissolved in acetone (3ml) was layered upon a solution of ligand **5.18** (22.8mg, 0.043mmol) in hot acetone (3ml). Immediately a small amount of blue precipitate began to form as the solution started to cool. After standing for a few weeks the blue crystalline solid was collected and filtered off. Yield 28.8mg (80.6%). M.p. 291-292°C. Anal. Found: C, 51.84; H, 4.77; N, 3.32. Calc. for $C_{36}H_{36}N_2O_2Cl_4Co_2.2½H_2O$: C, 51.88; H, 4.96; N, 3.36 revealing a M_2L complex.

With copper(II) chloride

A solution of copper(II) chloride (16.7mg, 0.097mmol) dissolved in methanol (5ml) was layered upon a solution of ligand **5.18** (24.5mg, 0.046mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting pale green solution gave a green precipitate that was collected by filtration and dried *in vacuo*. Yield 14mg

(45.4%). M.p. 241-245°C. Anal. Found: C, 64.20; H, 5.42; N, 4.05. Calc. for $C_{36}H_{36}N_2O_2Cl_2Cu.½H_2O$: C, 64.33; H, 5.55; N, 4.17 revealing a 1:1 complex.

With copper nitrate

A solution of copper nitrate (24.1mg, 0.10mmol) dissolved in methanol (5ml) was layered upon a solution of ligand **5.18** (26.4mg, 0.05mmol) dissolved in dichloromethane (5ml). The solution turned blue and a fine blue precipitate formed on standing. A few months later this was collected by filtration and dried *in vacuo*. Yield 29.9mg (40.1%). M.p. 220-224°C. Anal. Found: Anal. Found: C, 44.67; H, 4.59; N, 8.35. Calc. for $C_{36}H_{36}N_6O_{14}Cu_2.CH_2Cl_2.2CH_3OH$: C, 44.49; H, 4.40; N, 7.98 revealing a M_2L complex.

With copper perchlorate

Copper perchlorate (41.0mg, 0.11mmol) dissolved in methanol (5ml) was added to a solution of ligand **5.18** (29.5mg, 0.055mmol) dissolved in dichloromethane (5ml). Slow evaporation produced a blue solid. Yield 25.9mg (34.9%). Anal. Found: C, 64.48; H, 5.49; N, 4.12. Calc. for $C_{72}H_{72}N_4O_{12}Cl_2Cu.CH_3OH$: C, 64.86; H, 5.67; N, 4.14 revealing a ML_2 complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (42.0mg, 0.11mmol) in acetone (6ml) was layered upon a solution of ligand **5.18** (29.4mg, 0.055mmol) dissolved in hot acetone (5ml). Immediately an orange precipitate formed which was collected and dried *in vacuo*. Yield 29.7mg (72.1%). M.p. 270°C. Anal. Found: C, 57.62; H, 4.89; N, 3.67. Calc. for $C_{36}H_{36}N_2O_2Cl_2Pd.2½H_2O$: C, 57.57; H, 5.50; N, 3.73 revealing a 1:1 complex.

Complexes with 5.19

With copper chloride

A solution of copper chloride (17.1mg, 0.10mmol) dissolved in methanol (5ml) and layered upon a solution of ligand **5.19** (28.5mg, 0.05mmol) dissolved in dichloromethane (5ml). The solution turned pale green and a fine blue/green precipitate

formed on standing. This was collected by filtration and dried *in vacuo*. Yield 29.1mg (88%). M.p. 201-202°C. Anal. Found: C, 65.20; H, 5.58; N, 4.11. Calc. for $C_{36}H_{36}N_2O_2Cl_2Cu$: C, 65.20; H, 4.47; N, 4.22 revealing a 1:1 complex.

With copper perchlorate

A solution of copper perchlorate (41.4mg, 0.112mmol) dissolved in acetone (5ml) was layered upon a solution of ligand **5.19** (30.0mg, 0.056mmol) dissolved in chloroform (5ml). After a few minutes a greenish precipitate formed between the two layers. After a week the green crystalline precipitate was filtered off and found to be a fine crystalline solid. Yield 3.9mg (6.9%). M.p. 320-322°C. Anal. Found: C, 46.03; H, 4.42; N, 2.51. Calc. for $C_{36}H_{36}N_2O_{14}Cl_3Cu_2.(CH_3)_2CO$: C, 46.28; H, 4.18; N, 2.77 revealing a M_2L complex.

Preparation of complexes with the Bisphenol M ligands

Complexes with 5.22

With copper(II) chloride

A solution of copper(II) chloride (13.5mg, 0.079mmol) dissolved in methanol (5ml) was layered upon a solution of ligand **5.22** (18.4mg, 0.036mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting pale green solution produced a green precipitate that was collected by filtration and dried *in vacuo*. Yield 14.1mg (51.1%). M.p. 200-203°C. Anal. Found: C, 57.59; H, 5.48; N, 2.16. Calc. for $C_{34}H_{32}N_2O_2Cl_4Cu_2$: C, 53.07; H, 4.19; N, 3.64.

With palladium chloride

Palladium chloride (17.6mg, 0.099mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **5.22** (22.3mg, 0.045mmol). Immediately the solution went cloudy and a yellow precipitate began to form. A few weeks later the yellow precipitate was filtered off and dried *in vacuo*. Yield 22.8mg (38.9%). M.p. 291-293°C. Anal. Found: C, 65.27; H, 5.67; N, 4.81. Calc. for

$C_{68}H_{64}N_4O_4Cl_2Pd.(CH_3)_2CO.CH_2Cl_2$: C, 65.43; H, 5.49; N, 4.24 revealing a ML_2 complex.

Complexes with 5.23

With copper perchlorate, viz **5.31**

Copper perchlorate (40.0mg, 0.1mmol) was dissolved in acetone (5ml) and added to a solution of ligand **5.23** (27.0mg, 0.05mmol) dissolved in hot acetone (5ml). Slow evaporation of the solution over a week produced clusters of blue block-like crystals of **5.31** suitable for X-ray crystallography. X-ray analysis revealed an intriguing 'necklace' type structure composed of M_2L_2 squares. Yield 25.4mg (36.8%). M.p. 195-196°C. Anal. Found: C, 60.06; H, 5.24; N, 8.11. Calc. for $C_{64}H_{60}N_8O_8ClCu_2.2½H_2O.2(CH_3)_2CO$: C, 60.36; H, 5.57; N, 8.04.

With silver hexafluorophosphate, viz **5.32**

Ligand **5.23** (24.8mg, 0.049mmol) was dissolved in chloroform (2ml) and layered upon a solution of silver hexafluorophosphate (13.5mg, 0.053mmol) dissolved in acetone (2ml). Slow evaporation and vapour diffusion of diethyl ether into the reaction mixture gave colourless plate-like crystals of **5.32** suitable for X-ray crystallography which revealed an interesting silver polymer chain. Yield 12mg (21.5%). M.p. 247-250°C. Anal. Found: C, 39.33; H, 3.80; N, 5.10. Calc. for $C_{32}H_{30}N_4O_2PF_6Ag_2.3½H_2O.2(CH_3)_2CO$: C, 39.67; H, 4.29; N, 4.87.

With silver perchlorate, viz **5.33**

Ligand **5.23** (26.6mg, 0.053mmol) was dissolved in chloroform (2ml) and layered upon a solution of silver perchlorate (11.8mg, 0.057mmol) dissolved in acetone (2ml). Slow evaporation and vapour diffusion of diethyl ether into the reaction mixture gave colourless needle-like crystals suitable for X-ray crystallography. Yield 9.1mg (18.1%). M.p. 225°C. Anal. Found: C, 40.29; H, 3.36; N, 5.49. Calc. for $C_{32}H_{30}N_4O_{10}Cl_2Ag_2.2H_2O$: C, 40.32; H, 3.59; N, 5.88.

With copper(II) chloride

Copper(II) chloride (19.1mg, 0.11mmol) and ligand **5.23** (28.2mg, 0.056mmol) were both dissolved in hot methanol (10ml) and the solutions combined. On standing a green crystalline material precipitated from the reaction mixture, which was collected, washed with methanol and dried *in vacuo*. Yield 38.2mg (81.4%). M.p. 242°C. Anal. Found: C, 45.49; H, 4.31; N, 6.46. Calc. for $C_{32}H_{30}N_4O_2Cl_4Cu_2.4H_2O$: C, 45.56; H, 4.54; N, 6.64 revealing a M_2L complex.

With copper(I) iodide

A solution of copper(I) iodide (20.3mg, 0.10mmol) dissolved in acetonitrile (5ml) was carefully layered onto a solution of ligand **5.23** (27.1mg, 0.054mmol) dissolved in dichloromethane (5ml) to give a yellow solution. A yellow crystalline precipitate appeared on standing for a few weeks, which was filtered off and dried *in vacuo*. Yield 25.8mg (53.1%). M.p. 170-173°C. Anal. Found: C, 42.29; H, 3.60; N, 5.91. Calc. for $C_{32}H_{30}N_4O_2I_2Cu_2.H_2O$: C, 42.63; H, 3.58; N, 6.21 revealing a M_2L complex.

With palladium chloride

Palladium chloride (24.5mg, 0.138mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **5.23** (35.0mg, 0.069mmol). Immediately the solution went cloudy and a yellow precipitate began to form. A few weeks later the yellow precipitate was filtered off, washed with methanol and dried *in vacuo*. Yield 19.2mg (21.6%). M.p. 148-149°C. Anal. Found: C, 60.95; H, 4.92; N, 8.70. Calc. for $C_{32}H_{30}N_4O_2Cl_2Pd$: C, 59.64; H, 4.69; N, 8.69 revealing a ML complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (44.3mg, 0.12mmol) in acetone (6ml) was layered upon a solution of ligand **5.23** (29.1mg, 0.058mmol) dissolved in hot acetone (5ml). Immediately a yellow precipitate formed which was collected and dried *in vacuo*. Yield 36.7mg (78.9%). M.p. 275°C. Anal. Found: C, 47.70; H, 3.88; N, 6.76. Calc. for $C_{32}H_{30}N_4O_2Cl_2Pd_2.H_2O$: C, 47.78; H, 4.01; N, 6.97 revealing a M_2L complex.

Complexes with 5.24

With copper(II) chloride, viz **5.34**

A solution of copper(II) chloride (20.8mg, 0.12mmol) dissolved in methanol (5ml) was layered upon a solution of ligand **5.24** (36.4mg, 0.06mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting solution gave large blue crystalline plates of **5.34** suitable for X-ray crystallography. X-ray analysis revealed a 20-membered chelate ring. Yield 35.4mg (61.1%). M.p. 260-262°C. Anal. Found: C, 56.56; H, 4.70; N, 2.97. Calc. for $C_{42}H_{36}N_2O_6Cl_2Cu.2CH_2Cl_2.2CH_3OH.½H_2O$: C, 56.48; H, 5.05; N, 2.86.

With silver perchlorate, viz **5.35**

Ligand **5.24** (27.3mg, 0.045mmol) was dissolved in chloroform (2ml) and layered upon a solution of silver perchlorate (17.7mg, 0.085mmol) dissolved in acetone (2ml). Slow evaporation and vapour diffusion of diethyl ether into the reaction mixture gave large colourless block-like crystals of **5.35** suitable for X-ray crystallography. X-ray analysis revealed another example of a discrete 20-membered chelete ring. Yield 34.2mg (94.3%). M.p. 140-141°C. Anal. Found: C, 46.21; H, 3.64; N, 2.34. Calc. for $C_{42}H_{36}N_2O_6ClAg.3CHCl_3$: C, 46.35; H, 3.37; N, 2.40. .

With silver hexafluorophosphate, viz **5.36**

Ligand **5.24** (32.3mg, 0.054mmol) was dissolved in chloroform (2ml) and layered upon a solution of silver hexafluorophosphate (13.6mg, 0.054mmol) dissolved in acetone (2ml). Slow evaporation and vapour diffusion of diethyl ether into the reaction mixture gave large colourless block-like crystals of **5.36** suitable for X-ray crystallography. Yield 10.5mg (19%). M.p. 123°C. Anal. Found: C, 50.49; H, 3.55; N, 2.68. Calc. for $C_{42}H_{36}N_2O_4PF_2Ag.2CHCl_3$: C, 50.41; H, 3.65; N, 2.67.

With silver tetrafluoroborate, viz **5.37**

Ligand **5.24** (24.0mg, 0.040mmol) was dissolved in chloroform (2ml) and layered upon a solution of silver tetrafluoroborate (7.7mg, 0.040mmol) dissolved in acetone (2ml). Slow evaporation and vapour diffusion of diethyl ether into the reaction mixture gave colourless block-like crystals suitable for X-ray crystallography. Yield 15.6mg (39.4%).

M.p. 248-250°C. Anal. Found: C, 53.02; H, 3.96; N, 2.84. Calc. for $C_{42}H_{36}N_2O_2BF_4Ag.1⅔CHCl_3$: C, 52.74; H, 3.82; N, 2.82.

With palladium chloride

Palladium chloride (21.4mg, 0.118mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **5.24** (34.4mg, 0.057mmol) which gave an orange solution. After a week a fine orange crystalline solid formed that was filtered off and dried *in vacuo*. Yield 39.5mg (87.3%). M.p. 306-307°C. Anal. Found: C, 62.53; H, 4.81; N, 3.45. Calc. for $C_{42}H_{36}N_2O_2Cl_2Pd.1½H_2O$: C, 62.66; H, 4.88; N, 3.48 revealing a 1:1 complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (45.8mg, 0.12mmol) in acetone (6ml) was layered upon a solution of ligand **5.24** (36.1mg, 0.06mmol) dissolved in hot acetone (5ml). On standing for a day an orange precipitate formed. The precipitate was subsequently recrystallised from acetonitrile. Clusters of orange block-like crystals formed within a day of standing, which were collected and dried *in vacuo*. These crystals proved to be suitable for X-ray crystallography; however the structure was unable to be solved due to the crystals being highly twinned with stacks of thin plates stacked upon each other. Yield 32.5mg (61.5%). M.p. 295-297°C. Anal. Found: C, 59.67; H, 4.48; N, 4.64. Calc. for $C_{42}H_{36}N_2O_2Cl_2Pd.CH_3CN.3½H_2O$: C, 59.91; H, 5.26; N, 4.76 revealing a 1:1 complex.

Complexes with 5.25

With copper(I) iodide

A solution of copper(I) iodide (15.5mg, 0.08mmol) dissolved in acetonitrile (5ml) was carefully layered onto a solution of ligand **5.25** (24.2mg, 0.04mmol) dissolved in dichloromethane (5ml). After a few weeks a yellow solid appeared on standing that was filtered off. Yield 8.1mg (20.8%). M.p. 181°C. Anal. Found: C, 50.54; H, 3.69; N, 5.65. Calc. for $C_{40}H_{34}N_4O_2ICu.2½CH_2Cl_2$: C, 50.77; H, 3.91; N, 5.57 revealing a 1:1 complex.

With palladium chloride

Palladium chloride (18.4mg, 0.103mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol:dichloromethane solution of ligand **5.25** (28.9mg, 0.047mmol). A small amount of precipitate appeared at the boundary between the two solutions. A few weeks later the yellow precipitate was filtered off and dried *in vacuo*. Yield 6.6mg (18%). M.p. 296-299°C. Anal. Found: C, 61.34; H, 4.34; N, 7.17. Calc. for $C_{40}H_{34}N_4O_2Cl_2Pd$: C, 61.59; H, 4.39; N, 7.18 revealing a 1:1 complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (39.6mg, 0.104mmol) in acetone (6ml) was layered upon a solution of ligand **5.25** (31.3mg, 0.052mmol) dissolved in hot acetone (5ml). Immediately a yellow precipitate formed which was collected a week later and dried *in vacuo*. Yield 20.9mg (43.1%). M.p. 275-277°C. Anal. Found: C, 52.10; H, 3.88; N, 5.95. Calc. for $C_{40}H_{34}N_4O_2Cl_2Pd.2H_2O.CHCl_3$: C, 52.64; H, 4.20; N, 5.99 revealing a 1:1 complex.

Complexes with 5.38

With silver hexafluorophosphate, viz **5.41**

Ligand **5.38** (34.0mg, 0.064mmol) was dissolved in chloroform (2ml) and layered upon a solution of silver hexafluorophosphate (17.1mg, 0.066mmol) dissolved in acetone (2ml). Slow evaporation and vapour diffusion of diethyl ether into the reaction mixture gave clumps of colourless block-like crystals of **5.41** suitable for X-ray crystallography. Yield 26.9mg (53.9%). M.p. 202-204°C. Anal. Found: C, 50.20; H, 4.64; N, 3.07. Calc. for $C_{36}H_{36}N_2O_2PF_6Ag.CHCl_3.(CH_3)_2CO$: C, 50.10; H, 4.52; N, 2.92.

With silver perchlorate, viz **5.42**

Ligand **5.38** (30.9mg, 0.058mmol) was dissolved in chloroform (2ml) and layered upon a solution of silver perchlorate (11.4mg, 0.054mmol) dissolved in acetone (2ml). Slow evaporation and vapour diffusion of diethyl ether into the reaction mixture gave clumps of colourless block-like crystals of **5.42** suitable for X-ray crystallography which revealed another example of a dimetallic silver macrocycle. Yield 19.1mg (44.6%).

M.p. 202-205°C. Anal. Found: C, 51.76; H, 4.47; N, 3.23. Calc. for $C_{36}H_{36}N_2O_6ClAg.CHCl_3$: C, 51.95; H, 4.36; N, 3.27.

With silver trifluoromethanesulfonate, viz **5.43**

Ligand **5.38** (34.0mg, 0.064mmol) was dissolved in chloroform (2ml) and layered upon a solution of silver trifluoromethanesulfonate (17.1mg, 0.066mmol) dissolved in acetone (2ml). Slow evaporation and vapour diffusion of diethyl ether into the reaction mixture gave clumps of colourless block-like crystals of **5.43** suitable for X-ray crystallography. Yield 32.7mg (56.6%). M.p. 218°C. Anal. Found: C, 51.20; H, 4.30; N, 3.22. Calc. for $C_{37}H_{36}N_2O_5F_3SAg.CHCl_3.(CH_3)_2CO$: C, 51.13; H, 4.50; N, 2.91.

With silver tetrafluoroborate

Ligand **5.38** (29.8mg, 0.056mmol) was dissolved in chloroform (2ml) and layered upon a solution of silver tetrafluoroborate (11.2mg, 0.058mmol) dissolved in acetone (2ml). Slow evaporation and vapour diffusion of diethyl ether into the reaction mixture gave clumps of colourless plate-like crystals suitable for X-ray crystallography. Yield 20mg (47.9%). M.p. 224-225°C. Anal. Found: C, 58.50; H, 5.14; N, 3.62. Calc. for $C_{36}H_{36}N_2O_2BF_4Ag.H_2O$: C, 58.32; H, 5.17; N, 3.78.

With zinc bromide, viz **5.44**

Ligand **5.38** (46.9mg, 0.088mmol) and zinc bromide (40.0mg, 0.018mmol) were both dissolved in hot methanol (10ml), combined and left to cool. Immediately a crystalline precipitate formed providing colourless crystals of **5.44** suitable for X-ray crystallography that revealed a 1-dimensional helical polymer. Yield 30.2mg (45.8%). M.p. 259-261°C. Anal. Found: C, 56.84; H, 4.93; N, 3.69. Calc. for $C_{36}H_{36}N_2O_2Br_2Zn.CH_3OH$: C, 56.54; H, 5.13; N, 3.56.

With copper perchlorate

Copper perchlorate (69.0mg, 0.164mmol) dissolved in methanol (5ml) and added to a solution of ligand **5.38** (43.0mg, 0.081mmol) dissolved in dichloromethane (5ml). Slow evaporation produced a purple crystalline solid that was collected and dried *in vacuo*. Yield 38.2mg (35.3%). M.p. 200-201°C. Anal. Found: C, 64.34; H, 5.65; N, 4.14. Calc. for $C_{72}H_{72}N_4O_{12}Cl_2Cu.H_2O$: C, 64.64; H, 5.58; N, 4.19 revealing a ML_2 complex.

With palladium chloride

Palladium chloride (29.7mg, 0.167mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **5.38** (43.1mg, 0.082mmol). Immediately the solution went cloudy and a yellow precipitate began to form. A few weeks later the yellow precipitate was filtered off, washed with methanol and dried *in vacuo*. Yield 61.4mg (98.8%). M.p. 274°C. Anal. Found: C, 57.11; H, 5.23; N, 3.44. Calc. for $C_{36}H_{36}N_2O_2\ Cl_2Pd.3H_2O$: C, 56.89; H, 5.57; N, 3.69 revealing a 1:1 complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (48.0mg, 0.125mmol) in acetone (6ml) was layered upon a solution of ligand **5.38** (34.0mg, 0.064mmol) dissolved in hot acetone (5ml). Immediately a yellow precipitate formed which was collected and dried *in vacuo*. Yield 31mg (67.1%). M.p. 300°C. Anal. Found: C, 59.52; H, 5.03; N, 3.89. Calc. for $C_{36}H_{36}N_2O_2Cl_2Pd.H_2O$: C, 59.72; H, 5.29; N, 3.87 revealing a 1:1 complex.

Complexes with 5.39

With copper nitrate, viz **5.45**

A solution of copper nitrate (31.9mg, 0.132mmol) in methanol (5ml) was layered upon a solution of ligand **5.39** (33.7mg, 0.063mmol) in hot methanol (5ml). Slow evaporation of the resulting pale green solution gave blue block-like crystals of **5.45** suitable for X-ray crystallography. Yield 20.9mg (53.2%). M.p. 162°C. Anal. Found: C, 70.42; H, 7.24; N, 5.17. Calc. for $C_{36}H_{36}N_2O_2Cu.CH_3OH.½CH_3CN$: C, 70.83; H, 6.72; N, 5.36.

With zinc bromide, viz **5.46**

A solution of zinc bromide (34.0mg, 0.15mmol) in methanol (5ml) was layered upon a solution of ligand **5.39** (38.2mg, 0.07mmol) dissolved in dichloromethane (5ml). Slow evaporation of the resulting colourless solution produced colourless crystalline plates of **5.46** suitable for X-ray crystallography which revealed a polymeric complex. Yield 44.8mg (31.6%). M.p. 275-277°C. Anal. Found: C, 45.16; H, 4.65; N, 2.84. Calc. for $C_{72}H_{72}N_4O_4Br_4Zn_2.6H_2O.4¼CH_2Cl_2$: C, 45.32; H, 4.64; N, 2.75.

With zinc chloride, viz **5.47**

Zinc chloride (18.0mg, 0.13mmol) was dissolved in methanol (5ml) and layered upon a solution of ligand **5.39** (30.5mg, 0.058mmol) dissolved in dichloromethane (5ml). The solution was concentrated by slow evaporation to give a colourless crystalline solid with block-like crystals suitable for X-ray crystallography. Yield 25.1mg (32.7%). M.p. 166-170°C. Anal. Found: C, 61.43; H, 5.40; N, 3.89. Calc. for $C_{72}H_{72}N_4O_4Cl_4Zn_2.1¼CH_2Cl_2$: C, 61.26; H, 5.23; N, 3.90.

With copper(II) chloride

Copper(II) chloride (22.3mg, 0.13mmol) and ligand **5.39** (35.2mg, 0.066mmol) were both dissolved up in hot methanol (10ml). Immediately a green precipitate formed that was collected and washed with methanol. Yield 38.2mg (39.8%). M.p. 203-205°C. Anal. Found: C, 59.65; H, 5.31; N, 3.84. Calc. for $C_{72}H_{72}N_4O_4Cl_6Cu$: C, 59.20; H, 4.97; N, 3.84 revealing a M_3L_2 complex.

With palladium chloride

Palladium chloride (23.1mg, 0.13mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **5.39** (34.5mg, 0.065mmol). Immediately the solution went cloudy and a yellow precipitate began to form. A few weeks later the yellow precipitate was filtered off, washed with methanol and dried *in vacuo*. Yield 33.2mg (70.7%). M.p. 215°C. Anal. Found: C, 59.90; H, 5.26; N, 3.85. Calc. for $C_{36}H_{36}N_2O_2Cl_2Pd.H_2O$: C, 59.72; H, 5.29; N, 3.87 revealing a 1:1 complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (57.7mg, 0.152mmol) in acetone (6ml) was layered upon a solution of ligand **5.39** (40.2mg, 0.076mmol) dissolved in hot acetone (5ml). Immediately a orange precipitate formed which was collected, washed with acetone and dried *in vacuo*. Yield 49.1mg (38%). M.p. 250°C. Anal. Found: C, 54.30; H, 4.38; N, 5.01. Calc. for $C_{36}H_{36}N_2O_2Cl_2Pd.CHCl_3.(CH_3)_2CO$: C, 54.12; H, 4.72; N, 3.28 revealing a 1:1 complex.

Complexes with 5.40

With copper(II) chloride

Copper(II) chloride (17.3mg, 0.10mmol) and ligand **5.40** (27.2mg, 0.052mmol) were both dissolved up in hot methanol (10ml). Slow evaporation over a few weeks of the resulting green solution gave a pale green solid. Yield 25.6mg (58.4%). M.p. 215-217°C. Anal. Found: C, 53.13; H, 5.18; N, 3.52. Calc. for $C_{36}H_{36}N_2O_2Cl_4Cu_2.1½CH_3OH$: C, 53.26; H, 5.01; N, 3.31 revealing a M_2L complex.

With palladium chloride

Palladium chloride (20.2mg, 0.114mmol) was dissolved in 2M HCl (5ml) and added slowly to a hot methanol solution of ligand **5.40** (30.1mg, 0.057mmol). Immediately the solution went cloudy and a yellow precipitate began to form. A few weeks later the yellow precipitate was filtered off and dried *in vacuo*. Yield 27.5mg (66.8%). M.p. 200°C. Anal. Found: C, 59.88; H, 5.19; N, 3.73. Calc. for $C_{36}H_{36}N_2O_2Cl_2Pd.H_2O$: C, 59.72; H, 5.29; N, 3.87 revealing a 1:1 complex.

With bis(benzonitrile)palladium(II) dichloride

A solution of bis(benzonitrile)palladium(II) dichloride (67.5mg, 0.177mmol) in acetone (6ml) was layered upon a solution of ligand **5.40** (46.8mg, 0.089mmol) dissolved in hot acetone (5ml). The solution was concentrated to dryness to give a yellow crystalline solid, which was collected and dried *in vacuo*. Yield 66.8mg (48%). M.p. 240-242°C. Anal. Found: C, 54.30; H, 4.38; N, 3.20. Calc. for $C_{72}H_{72}N_4O_4Cl_6Pd_3$: C, 54.41; H, 4.57; N, 3.53 revealing a M_3L_2 complex.

Appendices

Appendix 1: Crystallography

Tables A1-A18 list the crystal data and X-ray experimental details for seventy crystal structures discussed in this thesis. Throughout the text, selected bond lengths and angle are discussed and listed under the appropriate figures, while the remaining distances and angles, as well as atomic coordinates, anisotropic displacement factors and hydrogen atom coordinates are available on request from the Department of Chemistry, University of Canterbury.

The data for the crystal structures in this thesis were collected on a Bruker-Nonius APEX II system using graphite monochromatised Mo Kα (λ = 0.71073Å) radiation at the temperature indicated in the following tables. The data collection, cell determination and data reduction were all performed with the APEX software. All structures had intensities corrected for Lorentz and polarization effects and for adsorption using SADABS. All structures were solved by direct methods using SHELXS and refined on F^2 using all data by full-matrix least squares procedures using SHELXL-97. Unless otherwise stated all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 and 1.5 times the isotropic equivalent of their carrier carbon atoms. Some of the refinements reported may change a little upon preparation for final publication.

Table A1. Crystal data and structure refinement for 2.19, 2.21, 2.23 and 2.25.

Compound	**2.19**	**2.21**	**2.23**	**2.25**
Empirical formula	$C_{25}H_{22}N_2O_2$	$C_{23}H_{20}N_4O_2$	$C_{33}H_{26}N_2O_2$	$C_{31}H_{24}N_4O_2$
Formula weight	382.45	384.43	482.56	484.54
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	C2/c	$P2_1/c$	$P2_1/n$
Unit cell dimensions: a (Å)	9.8228(3)	22.4534(7)	12.8182(6)	6.0086(2)
b (Å)	11.5973(3)	11.5765(4)	10.0414(6)	18.8301(7)
c (Å)	17.5515(5)	7.7432(2)	19.9354(11)	21.2135(8)
α (°)	90	90	90	90
β (°)	92.990(1)	105.506(1)	92.768(2)	91.968(2)
γ (°)	90	90	90	90
Volume ($Å^3$)	1996.7(1)	1939.5(1)	2562.9(2)	2398.7(2)
Z	4	4	4	4
Density (calculated) (Mg/m^3)	1.272	1.317	1.251	1.342
Absorption coefficient (mm^{-1})	0.081	0.087	0.078	0.086
F(000)	808	808	1016	1016
Crystal size (mm^3)	0.50 x 0.35 x 0.10	0.75 x 0.15 x 0.05	0.75 x 0.10 x 0.04	0.59 x 0.25 x 0.02
Theta range for data collection (°)	2.11 to 30.13	2.00 to 25.05	1.59 to 25.05	2.89 to 25.05
Reflections collected	28891	21771	39165	29087
Independent reflections [R(int)]	5796 [0.0442]	1701 [0.0256]	4450 [0.0470]	4248 [0.0407]
Completeness to theta (°/%)	25.05 / 99.9	25.05 / 99.9	25.05 / 98.2	25.05 / 99.9
Data / restraints / parameters	5796 / 0 / 262	1707 / 0 / 133	4450 / 0 / 334	4248 / 0 / 336
Goodness-of-fit on F^2	0.964	1.066	0.975	1.020
Final R_1 [I>2sigma(I)]	0.0447	0.0312	0.0365	0.0306
wR_2 (all data)	0.1052	0.0810	0.0871	0.0738
Largest diff. peak and hole ($e.Å^{-3}$)	0.340 and -0.245	0.238 and -0.166	0.198 and -0.205	0.181 and -0.179

Table A2. Crystal data and structure refinement for 2.35, 2.36, 2.37 and 2.38.

Compound	**2.35**	**2.36**	**2.37**	**2.38**
Empirical formula	$C_{28}H_{28}N_2O_3Br_2Co$	$C_{28}H_{28}N_2O_3Cl_2Co$	$C_{25.5}H_{23}N_2O_2Cl_3Cu$	$C_{27}H_{25.5}N_4O_{8.5}Cl_{1.5}Cu$
Formula weight	659.27	570.35	559.35	658.73
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	Pbca	C2/c	C2/c	P-1
Unit cell dimensions: a (Å)	16.8279(4)	10.1300(2)	25.6493(7)	7.6612(3)
b (Å)	14.2016(3)	22.5373(5)	11.8168(4)	12.9798(5)
c (Å)	23.2998(5)	11.8858(2)	17.7522(5)	15.3372(6)
α (°)	90	90	90	91.364(2)
β (°)	90	91.854(1)	115.757(1)	103.816(2)
γ (°)	90	90	90	93.424(3)
Volume ($Å^3$)	5568.3(2)	2712.14(9)	4846.0(3)	1477.2(1)
Z	8	4	8	2
Density (calculated) (Mg/m^3)	1.573	1.397	1.533	1.481
Absorption coefficient (mm^{-1})	3.518	0.862	1.259	0.931
F(000)	2648	1180	2288	676
Crystal size (mm^3)	0.50 x 0.15 x 0.10	0.50 x 0.18 x 0.04	0.35 x 0.15 x 0.05	0.54 x 0.20 x 0.03
Theta range for data collection (°)	2.42 to 25.05	2.49 to 25.05	1.76 to 25.05	3.15 to 25.05
Reflections collected	64689	16441	34828	11550
Independent reflections [R(int)]	4930 [0.0553]	2363 [0.0424]	4208 [0.0425]	5182 [0.0255]
Completeness to theta (°/%)	25.05 / 99.9	25.05 / 98.1	25.05 / 98.2	25.05 / 98.8
Data / restraints / parameters	4930 / 0 / 325	2363 / 0 / 173	4208 / 0 / 312	5182 / 0 / 407
Goodness-of-fit on F^2	0.888	1.069	1.050	1.052
Final R_1 [I>2sigma(I)]	0.0249	0.0306	0.0290	0.0542
wR_2 (all data)	0.0713	0.0818	0.0758	0.1269
Largest diff. peak and hole ($e.Å^{-3}$)	0.520 and -0.427	0.382 and -0.373	0.783 and -0.797	1.167 and -0.814

Table A3. Crystal data and structure refinement for 2.39a, 2.39b, 2.40 and 2.41.

Compound	**2.39a**	**2.39b**	**2.40**	**2.41**
Empirical formula	$C_{25}H_{22}N_4O_8Cu$	$C_{100}H_{92}N_8O_{10}Cu_2$	$C_{28}H_{28}N_2O_3F_6PAg$	$C_{26}H_{22}N_2O_5F_3SAg$
Formula weight	570.01	1692.90	693.36	639.39
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	C2/c	C2/c	P-1	Cc
Unit cell dimensions: a (Å)	25.339(2)	25.515(2)	10.3043(6)	32.304(4)
b (Å)	19.5489(14)	19.6829(13)	11.4792(7)	10.6367(13)
c (Å)	22.3013(14)	22.1385(15)	13.1123(8)	18.2209(19)
α (°)	90	90	106.443(3)	90
β (°)	106.913(2)	105.915(4)	95.410(3)	123.311(6)
γ (°)	90	90	102.308(3)	90
Volume ($Å^3$)	10569.2(2)	10692.0(2)	1433.4(2)	5232.2(10)
Z	16	4	2	8
Density (calculated) (Mg/m^3)	1.433	1.052	1.606	1.623
Absorption coefficient (mm^{-1})	0.881	0.451	0.831	0.911
F(000)	4688	3544	700	2576
Crystal size (mm^3)	0.31 x 0.32 x 0.06	0.53 x 0.29 x 0.02	0.21 x 0.20 x 0.10	0.15 x 0.15 x 0.01
Theta range for data collection (°)	1.34 to 25.05	1.66 to 25.05	1.64 to 25.05	2.22 to 25.05
Reflections collected	50156	47947	19876	30932
Independent reflections [R(int)]	9310 [0.0978]	9458 [0.1063]	4977 [0.0336]	9260 [0.1745]
Completeness to theta (°/%)	25.05 / 99.6	25.05 / 99.9	25.05 / 97.7	25.05 / 99.9
Data / restraints / parameters	9310 / 0 / 688	9458 / 0 / 550	4977 / 0 / 370	9260 / 10 / 689
Goodness-of-fit on F^2	1.479	0.834	1.056	0.809
Final R_1 [I>2sigma(I)]	0.1279	0.0718	0.0268	0.0711
wR_2 (all data)	0.3825	0.1844	0.0650	0.1583
Largest diff. peak and hole ($e.Å^{-3}$)	1.805 and -2.089	0.860 and -0.700	0.983 and -0.533	1.316 and -1.184

Table A4. Crystal data and structure refinement for 2.42, 2.43, 2.44 and 2.45.

Compound	**2.42**	**2.43**	**2.44**	**2.45**
Empirical formula	$C_{25.5}H_{22}N_2O_{2.50}Br_2Zn$	$C_{27}H_{30}N_2O_4Cl_2Zn$	$C_{24}H_{24}N_4O_3Cl_2Cu$	$C_{27}H_{26}N_2O_2$
Formula weight	621.64	582.80	550.91	410.50
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	P-1	P-1	C2/c
Unit cell dimensions: a (Å)	11.6348(13)	9.8031(4)	7.7604(15)	17.6402(12)
b (Å)	17.997(2)	11.8600(6)	9.8959(19)	6.3584(4)
c (Å)	12.5088(12)	12.6413(6)	16.071(3)	18.7512(13)
α (°)	90	80.815(2)	84.843(12)	90
β (°)	95.269(6)	81.439(2)	79.438(12)	92.154(2)
γ (°)	90	69.315(2)	81.053(12)	90
Volume ($Å^3$)	2608.1(5)	1350.5(1)	1196.2(4)	2101.7(2)
Z	4	2	2	4
Density (calculated) (Mg/m^3)	1.583	1.433	1.530	1.297
Absorption coefficient (mm^{-1})	4.032	1.142	1.171	0.082
F(000)	1236	604	566	872
Crystal size (mm^3)	0.15 x 0.15 x 0.01	0.50 x 0.45 x 0.20	0.15 x 0.12 x 0.04	0.58 x 0.23 x 0.13
Theta range for data collection (°)	1.99 to 25.05	1.64 to 25.05	2.09 to 25.05	2.17 to 27.49
Reflections collected	25997	30549	16659	8466
Independent reflections [R(int)]	4614 [0.1055]	4758 [0.0339]	4227 [0.0957]	12395 [0.0191]
Completeness to theta (°/%)	25.05 / 100.0	25.05 / 99.5	25.05 / 99.9	27.49 / 99.0
Data / restraints / parameters	4614 / 0 / 317	4758 / 0 / 333	4227 / 2 / 314	2395 / 0 / 141
Goodness-of-fit on F^2	0.896	1.193	1.004	1.046
Final R_1 [I>2sigma(I)]	0.0449	0.0593	0.0574	0.0415
wR_2 (all data)	0.0823	0.1756	0.1483	0.1046
Largest diff. peak and hole ($e.Å^{-3}$)	0.574 and -0.642	2.034 and -0.656	0.779 and -1.168	0.341 and -0.238

Table A5. Crystal data and structure refinement for 2.47, 2.50, 2.51 and 2.54.

Compound	**2.47**	**2.50**	**2.51**	**2.54**
Empirical formula	$C_{27}H_{26}N_2O_2$	$C_{27}H_{26}N_2O_2Br_2Zn$	$C_{54}H_{52}N_8O_{16}Cu_2$	$C_{26}H_{24}N_4O_2$
Formula weight	410.50	635.69	1196.12	424.49
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	P-1	$P2_1/c$	P-1	$P2_1/c$
Unit cell dimensions: a (Å)	6.3060(2)	18.2385(13)	6.7551(3)	15.6096(10)
b (Å)	12.2921(3)	8.3922(6)	7.5031(4)	9.3870(7)
c (Å)	14.2864(4)	17.9674(12)	28.7363(14)	14.6695(11)
α (°)	92.837(1)	90	96.120(4)	90
β (°)	99.980(1)	113.083(2)	92.457(4)	100.607(3)
γ (°)	96.315(1)	90	111.196(3)	90
Volume ($Å^3$)	1081.36(5)	2529.9(3)	1344.99(11)	2112.8(3)
Z	2	4	1	4
Density (calculated) (Mg/m^3)	1.261	1.669	1.477	1.335
Absorption coefficient (mm^{-1})	0.080	4.157	0.869	0.087
F(000)	436	1272	618	896
Crystal size (mm^3)	0.62 x 0.30 x 0.30	0.40 x 0.35 x 0.01	0.28 x 0.26 x 0.02	0.48 x 0.40 x 0.12
Theta range for data collection (°)	1.67 to 25.05	2.46 to 25.05	0.72 to 25.05	1.33 to 25.05
Reflections collected	12392	13474	15748	18254
Independent reflections [R(int)]	3830 [0.0103]	4443 [0.0643]	4644 [0.0579]	3742 [0.0559]
Completeness to theta (°/%)	25.05 / 99.7	25.05 / 99.5	25.05 / 98.0	25.05 / 100.0
Data / restraints / parameters	3830 / 0 / 280	4443 / 0 / 307	4644 / 0 / 364	3742 / 0 / 289
Goodness-of-fit on F^2	1.057	0.0935	1.084	0.997
Final R_1 [I>2sigma(I)]	0.0322	0.0352	0.0663	0.0460
wR_2 (all data)	0.0860	0.0605	0.1787	0.1041
Largest diff. peak and hole ($e.Å^{-3}$)	0.227 and -0.184	0.846 and -0.551	0.819 and -0.532	0.223 and -0.250

Table A6. Crystal data and structure refinement for 2.55, 2.56, 2.61 and 2.62.

Compound	**2.55**	**2.56**	**2.61**	**2.62**
Empirical formula	$C_{36}H_{30}N_2O_2S$	$C_{34}H_{28}N_4O_2$	$C_{28}H_{26}N_2O_2Cl_2Co$	$C_{28.25}H_{27}N_2O_{2.50}Cl_2Cu$
Formula weight	554.68	524.60	552.34	564.96
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	P-1	P-1	$P2_1/n$
Unit cell dimensions: a (Å)	8.3728(6)	6.0550(2)	10.083(2)	16.3502(7)
b (Å)	33.712(3)	12.6334(5)	12.140(3)	13.6419(7)
c (Å)	10.6633(8)	17.8573(7)	13.015(2)	24.9954(13)
α (°)	90	73.580(2)	94.311(12)	90
β (°)	93.069(4)	84.141(2)	112.356(12)	106.310(2)
γ (°)	90	81.180(2)	91.965(12)	90
Volume ($Å^3$)	3005.5(4)	1292.30(8)	1465.8(5)	5350.8(5)
Z	4	2	2	8
Density (calculated) (Mg/m^3)	1.226	1.348	1.251	1.403
Absorption coefficient (mm^{-1})	0.142	0.085	0.793	1.045
F(000)	1168	552	570	2332
Crystal size (mm^3)	0.60 x 0.36 x 0.35	0.70 x 0.15 x 0.03	0.40 x 0.08 x 0.04	0.55 x 0.12 x 0.08
Theta range for data collection (°)	1.21 to 25.05	2.52 to 25.05	1.69 to 26.66	1.34 to 25.05
Reflections collected	38415	9017	19076	95759
Independent reflections [R(int)]	5315 [0.0267]	4500 [0.0187]	5797 [0.1485]	9450 [0.0386]
Completeness to theta (°/%)	25.05 / 100.0	25.05 / 98.3	26.66 / 93.5	25.05 / 99.6
Data / restraints / parameters	5315 / 0 / 421	4500 / 0 / 361	5797 / 0 / 390	9450 / 0 / 650
Goodness-of-fit on F^2	1.583	1.027	1.205	1.020
Final R_1 [I>2sigma(I)]	0.0467	0.0338	0.1074	0.0272
wR_2 (all data)	0.1772	0.0844	0.2586	0.0672
Largest diff. peak and hole ($e.Å^{-3}$)	0.619 and -0.206	0.296 and -0.186	2.108 and -1.190	0.371 and -0.405

Table A7. Crystal data and structure refinement for 2.63, 2.64, 2.65 and 2.66.

Compound	**2.63**	**2.64**	**2.65**	**2.66**
Empirical formula	$C_{28}H_{26}N_2O_2Br_2Cl_2Zn$	$C_{56}H_{56}N_4O_7Cl_4Zn_2$	$C_{26}H_{24}N_4O_2ICu$	$C_{52}H_{48}N_8O_4Br_2Co$
Formula weight	718.60	1163.92	614.93	1067.73
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P-1	C2/c	C2/c
Unit cell dimensions: a (Å)	9.9906(12)	9.762(3)	19.5566(11)	20.1622(5)
b (Å)	12.2796(12)	12.209(4)	16.6668(11)	16.1512(4)
c (Å)	13.0727(14)	12.984(4)	15.3070(9)	14.9275(4)
α (°)	84.100(6)	84.078(9)	90	90
β (°)	68.575(5)	69.011(9)	106.861(2)	113.240(1)
γ (°)	86.625(7)	85.588(10)	90	90
Volume ($Å^3$)	1484.6(3)	1435.8(8)	4774.8(5)	4466.6(2)
Z	2	1	8	4
Density (calculated) (Mg/m^3)	1.607	1.356	1.711	1.588
Absorption coefficient (mm^{-1})	3.726	1.066	2.240	2.232
F(000)	716	601	2448	2180
Crystal size (mm^3)	0.50 x 0.19 x 0.05	0.15 x 0.10 x 0.01	0.34 x 0.10 x 0.05	0.21 x 0.20 x 0.01
Theta range for data collection (°)	1.68 to 25.05	2.47 to 25.05	1.64 to 25.05	1.93 to 25.05
Reflections collected	20167	8182	36721	19403
Independent reflections [R(int)]	5119 [0.0927]	4928 [0.1014]	4211 [0.0308]	3952 [0.0337]
Completeness to theta (°/%)	25.05 / 97.1	25.05 / 96.8	25.05 / 99.6	25.05 / 99.6
Data / restraints / parameters	5119 / 0 / 359	4928 / 0 / 335	4211 / 0 / 307	3952 / 0 / 303
Goodness-of-fit on F^2	1.115	0.955	1.016	1.034
Final R_1 [I>2sigma(I)]	0.0789	0.0897	0.0161	0.0234
wR_2 (all data)	0.1889	0.2071	0.0392	0.0599
Largest diff. peak and hole ($e.Å^{-3}$)	3.631 and -1.478	2.019 and -0.811	0.445 and -0.438	0.546 and -0.245

Table A8. Crystal data and structure refinement for 2.70, 2.71, 2.72 and 2.73.

Compound	**2.70**	**2.71**	**2.72**	**2.73**
Empirical formula	$C_{30}H_{30}N_2O_2Cl_2Zn$	$C_{31}H_{32}N_2O_2Cl_2CuI$	$C_{33}H_{39.5}N_4O_{10.75}ClCu_2$	$C_{30}H_{30}N_2O_2Br_2Zn$
Formula weight	586.83	725.93	808.99	675.75
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	P-1	$P2_1/n$	$P2_1/c$
Unit cell dimensions: a (Å)	15.4297(14)	9.7293(3)	7.9957(8)	9.4289(6)
b (Å)	8.6644(8)	11.7545(5)	21.728(2)	17.8957(13)
c (Å)	23.048(2)	13.3384(5)	20.119(2)	16.3571(11)
α (°)	90	86.104(1)	90	90
β (°)	99.112(5)	83.767(1)	95.323(3)	96.384(3)
γ (°)	90	78.144(1)	90	90
Volume ($Å^3$)	3042.4(5)	1482.4(1)	3480.2(6)	2742.9(3)
Z	4	2	4	4
Density (calculated) (Mg/m^3)	1.281	1.626	1.544	1.636
Absorption coefficient (mm^{-1})	1.010	1.990	1.325	3.839
F(000)	1216	728	1672	1360
Crystal size (mm^3)	0.55 x 0.14 x 0.05	0.30 x 0.13 x 0.02	0.34 x 0.34 x 0.10	0.45 x 0.18 x 0.05
Theta range for data collection (°)	1.34 to 25.05	1.54 to 25.05	1.38 to 27.50	1.69 to 27.20
Reflections collected	20783	15720	20351	43417
Independent reflections [R(int)]	5383 [0.2209]	5181 [0.0334]	7851 [0.0461]	6051 [0.0479]
Completeness to theta (°/%)	25.05 / 99.9	25.05 / 98.9	27.50 / 98.1	25.05 / 99.9
Data / restraints / parameters	5383 / 0 / 370	5181 / 0 / 362	7851 / 0 / 482	6051 / 0 / 334
Goodness-of-fit on F^2	1.023	1.088	1.021	0.957
Final R_1 [I>2sigma(I)]	0.0967	0.0476	0.0451	0.0329
wR_2 (all data)	0.1785	0.1371	0.0999	0.0763
Largest diff. peak and hole ($e.Å^{-3}$)	0.832 and -0.765	1.754 and -2.478	0.510 and -0.437	1.364 and -0.674

Table A9. Crystal data and structure refinement for 2.74, 3.2, 3.3 and 3.5.

Compound	**2.74**	**3.2**	**3.3**	**3.5**
Empirical formula	$C_{30}H_{30}N_2O_2Cl_2Zn$	$C_{30}H_{24}N_2O_2$	$C_{28}H_{22}N_4O_2$	$C_{36}H_{26}N_4O_2$
Formula weight	586.83	444.51	446.50	546.61
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$Pna2_1$	$P2_1/n$
Unit cell dimensions: a (Å)	15.6926(6)	13.5894(7)	11.9263(4)	7.2242(3)
b (Å)	10.7146(4)	11.9003(5)	24.9819(7)	31.7205(13)
c (Å)	17.5701(7)	15.2111(7)	7.4723(2)	11.9072(5)
α (°)	90	90	90	90
β (°)	113.567(2)	105.038(3)	90	95.642(2)
γ (°)	90	90	90	90
Volume ($Å^3$)	2707.8(2)	2375.7(2)	2226.3(1)	2715.4(2)
Z	4	4	4	4
Density (calculated) (Mg/m^3)	1.439	1.243	1.332	1.337
Absorption coefficient (mm^{-1})	1.135	0.078	0.086	0.085
F(000)	1216	936	936	1144
Crystal size (mm^3)	0.61 x 0.60 x 0.01	0.34 x 0.21 x 0.08	0.60 x 0.09 x 0.01	0.90 x 0.40 x 0.03
Theta range for data collection (°)	2.83 to 25.05	2.20 to 25.05	2.85 to 25.04	2.91 to 25.05
Reflections collected	24235	22115	25960	18387
Independent reflections [R(int)]	4791 [0.0362]	4213 [0.0498]	2131 [0.0586]	4804 [0.0280]
Completeness to theta (°/%)	25.05 / 99.8	25.05 / 99.9	25.04 / 99.9	25.05 / 99.8
Data / restraints / parameters	4791 / 0 / 334	4213 / 0 / 308	2131 / 1 / 307	4804 / 0 / 379
Goodness-of-fit on F^2	1.018	0.996	1.050	1.020
Final R_1 [I>2sigma(I)]	0.0269	0.0391	0.0273	0.0392
wR_2 (all data)	0.0715	0.0968	0.0613	0.0919
Largest diff. peak and hole ($e.Å^{-3}$)	0.532 and -0.442	0.278 and -0.205	0.133 and -0.158	0.237 and -0.153
Flack parameter (if applicable)			0.0(10)	

Table A10. Crystal data and structure refinement for 3.8, 4.15, 4.16 and 4.17.

Compound	**3.8**	**4.15**	**4.16**	**4.17**
Empirical formula	$C_{31}H_{25}N_2O_2F_6PCl_3Ag$	$C_{35}H_{27}N_3O_3$	$C_{32}H_{24}N_6O_3$	$C_{48}H_{35}N_3O_3Cl_2$
Formula weight	710.65	537.60	540.57	772.69
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic
Space group	C2/c	$P6_3$	P-1	P-1
Unit cell dimensions: a (Å)	17.0402(10)	14.0521(3)	10.1019(3)	9.851(3)
b (Å)	11.0732(7)	14.0521(3)	12.0338(4)	9.980(3)
c (Å)	31.3066(19)	8.1827(5)	12.9231(7)	22.268(7)
α (°)	90	90	103.604(2)	84.289(16)
β (°)	98.671(3)	90	109.209(2)	84.171(17)
γ (°)	90	90	108.662(2)	64.281(15)
Volume ($Å^3$)	5839.7(6)	1399.3(1)	1299.76(6)	1958.4(10)
Z	8	2	2	2
Density (calculated) (Mg/m^3)	1.617	1.276	1.381	1.310
Absorption coefficient (mm^{-1})	0.849	0.082	0.092	0.213
F(000)	2851	564	564	804
Crystal size (mm^3)	0.40 x 0.25 x 0.04	0.70 x 0.25 x 0.05	0.52 x 0.15 x 0.15	0.60 x 0.35 x 0.30
Theta range for data collection (°)	1.32 to 25.05	2.90 to 27.45	2.26 to 25.05	0.92 to 25.04
Reflections collected	37726	20714	20367	26977
Independent reflections [R(int)]	5174 [0.1015]	1141 [0.0845]	4610 [0.0330]	6919 [0.3811]
Completeness to theta (°/%)	25.05 / 100.0	27.45 / 99.4	25.05 / 99.9	25.04 / 99.9
Data / restraints / parameters	5174 / 0 / 399	1141 / 1 / 167	4610 / 0 / 371	6919 / 0 / 505
Goodness-of-fit on F^2	1.392	1.028	1.050	1.220
Final R_1 [I>2sigma(I)]	0.0699	0.0430	0.0321	0.2243
wR_2 (all data)	0.1927	0.1168	0.0792	0.4680
Largest diff. peak and hole ($e.Å^{-3}$)	1.659 and -0.936	0.402 and -0.222	0.170 and -0.208	0.932 and -0.957
Flack parameter (if applicable)		0.0(10)		

Table A11. Crystal data and structure refinement for 4.18, 4.22, 4.23 and 4.24.

Compound	**4.18**	**4.22**	**4.23**	**4.24**
Empirical formula	$C_{44}H_{30}N_6O_3$	$C_{35}H_{27}N_3O_3Cl_2Cu$	$C_{32}H_{24}N_6O_3CuI$	$C_{39}H_{33}N_3O_3$
Formula weight	690.74	672.04	731.01	591.68
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1	P-1
Unit cell dimensions: a (Å)	6.181(9)	14.6326(6)	9.6880(3)	6.7134(4)
b (Å)	19.54(2)	14.9555(6)	11.6176(3)	13.0108(9)
c (Å)	19.59(3)	20.3588(8)	15.5338(4)	19.2362(16)
α (°)	60.71(3)	73.463(2)	94.725(1)	109.752(2)
β (°)	88.81(4)	86.794(2)	102.505(1)	94.467(3)
γ (°)	89.36(4)	88.622(2)	106.969(1)	96.779(2)
Volume ($Å^3$)	2063(5)	4264.2(3)	1612.60(8)	1557.8(2)
Z	2	5	2	2
Density (calculated) (Mg/m^3)	1.112	1.309	1.505	1.261
Absorption coefficient (mm^{-1})	0.072	0.834	1.675	0.080
F(000)	720	1725	728	624
Crystal size (mm^3)	0.35 x 0.30 x 0.02	0.50 x 0.49 x 0.18	0.25 x 0.10 x 0.09	0.62 x 0.17 x 0.04
Theta range for data collection (°)	1.21 to 25.05	1.04 to 25.05	1.36 to 30.50	1.13 to 25.05
Reflections collected	9070	60491	22565	14729
Independent reflections [R(int)]	6368 [0.2262]	15072 [0.0618]	9622 [0.0560]	5491 [0.0426]
Completeness to theta (°/%)	25.05 / 86.8	25.05 / 99.7	30.05 / 97.8	25.05 / 99.9
Data / restraints / parameters	6368 / 0 / 478	15072 / 0 / 908	9622 / 0 / 389	5491 / 0 / 417
Goodness-of-fit on F^2	1.827	4.284	0.938	1.114
Final R_1 [I>2sigma(I)]	0.2214	0.2108	0.0448	0.0553
wR_2 (all data)	0.5375	0.5266	0.1329	0.1517
Largest diff. peak and hole ($e.Å^{-3}$)	0.910 and -1.121	5.303 and -2.646	2.294 and -1.031	0.904 and -0.653

Table A12. Crystal data and structure refinement for 4.33, 4.35, 5.10 and 5.12.

Compound	**4.33**	**4.35**	**5.10**	**5.12**
Empirical formula	$C_{41}H_{36}N_4O_4$	$C_{57}H_{44}N_4O_4$	$C_{17}H_{16}NO$	$C_{42}H_{36}N_2O_2$
Formula weight	648.74	848.96	250.31	600.73
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/c$	Pnn2	C2/c	$P2_1/c$
Unit cell dimensions: a (Å)	16.6512(5)	11.1349(3)	22.4264(13)	6.2060(2)
b (Å)	10.3247(3)	18.1266(4)	11.6810(7)	20.7515(6)
c (Å)	21.1705(5)	11.1145(2)	12.0145(6)	11.8633(4)
α (°)	90	90	90	90
β (°)	112.797(1)	90	119.393(3)	96.352(2)
γ (°)	90	90	90	90
Volume ($Å^3$)	3355.3(2)	2243.33(9)	2742.2(3)	1518.42(8)
Z	4	2	4	2
Density (calculated) (Mg/m^3)	1.284	1.257	0.606	1.314
Absorption coefficient (mm^{-1})	0.084	0.079	0.038	0.080
F(000)	1368	892	532	636
Crystal size (mm^3)	0.45 x 0.35 x 0.10	0.45 x 0.43 x 0.08	0.50 x 0.09 x 0.03	0.50 x 0.15 x 0.04
Theta range for data collection (°)	2.38 to 25.05	2.59 to 25.05	2.03 to 25.05	2.61 to 25.05
Reflections collected	51569	23598	13406	18150
Independent reflections [R(int)]	5942 [0.0414]	2106 [0.0491]	2425 [0.0958]	2690 [0.0765]
Completeness to theta (°/%)	25.05 / 99.9	25.05 / 99.9	25.05 / 99.8	25.05 / 99.9
Data / restraints / parameters	5942 / 0 / 442	2106 / 1 / 294	2425 / 0 / 172	2690 / 0 / 210
Goodness-of-fit on F^2	1.043	1.048	0.872	0.926
Final R_1 [I>2sigma(I)]	0.0447	0.0261	0.0544	0.0362
wR_2 (all data)	0.1163	0.0683	0.1190	0.0775
Largest diff. peak and hole ($e.Å^{-3}$)	0.599 and -0.602	0.165 and -0.213	0.236 and -0.231	0.237 and -0.224
Flack parameter (if applicable)		0.0(10)		

Table A13. Crystal data and structure refinement for 5.14, 5.15, 5.16 and 5.17.

Compound	**5.14**	**5.15**	**5.16**	**5.17**
Empirical formula	$C_{37}H_{32}N_{2.50}O_{2.50}Br_2Co$	$C_{142}H_0N_8O_{10}Cl_8Co_4$	$C_{112}H_0N_{12}O_6Cl_6Cu_3$	$C_{36}H_{38}N_2O_3$
Formula weight	770.40	2497.83	2012.56	546.68
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	C2/c	P-1	P-1	P-1
Unit cell dimensions: a (Å)	7.4905(3)	12.8959(11)	7.2555(7)	6.1610(4)
b (Å)	32.1871(13)	16.7068(16)	21.390(2)	6.7560(4)
c (Å)	15.1800(6)	17.5019(17)	22.182(2)	17.4925(11)
α (°)	90	74.465(5)	66.692(6)	79.075(5)
β (°)	91.076(2)	69.971(5)	82.090(7)	85.244(4)
γ (°)	90	70.214(5)	85.534(6)	87.610(4)
Volume ($Å^3$)	3659.2(3)	3284.0(5)	3130.5(5)	712.19(8)
Z	4	1	1	1
Density (calculated) (Mg/m^3)	1.398	1.263	1.068	1.275
Absorption coefficient (mm^{-1})	2.688	0.718	0.681	0.081
F(000)	1554	1233	993	292
Crystal size (mm^3)	0.65 x 0.44 x 0.10	0.60 x 0.35 x 0.19	0.35 x 0.25 x 0.02	0.40 x 0.19 x 0.03
Theta range for data collection (°)	1.27 to 25.05	1.26 to 25.05	1.01 to 25.05	3.07 to 26.39
Reflections collected	24058	49306	36247	10353
Independent reflections [R(int)]	3244 [0.0420]	11616 [0.0938]	10788 [0.1905]	2887 [0.0423]
Completeness to theta (°/%)	25.05 / 99.8	25.05 / 99.7	25.05 / 97.0	26.39 / 98.4
Data / restraints / parameters	3244 / 0 / 233	11616 / 0 / 775	10788 / 0 / 271	2887 / 0 / 190
Goodness-of-fit on F^2	1.285	3.944	2.058	1.026
Final R_1 [I>2sigma(I)]	0.0272	0.1830	0.1811	0.0588
wR_2 (all data)	0.0886	0.5078	0.4569	0.1481
Largest diff. peak and hole ($e.Å^{-3}$)	0.753 and -0.467	4.401 and -1.264	1.333 and -2.181	0.287 and -0.351

Table A14. Crystal data and structure refinement for 5.18, 5.19, 5.20 and 5.23.

Compound	**5.18**	**5.19**	**5.20**	**5.23**
Empirical formula	$C_{36}H_{36}N_2O_2$	$C_{36}H_{36}N_2O_2$	$C_{43}H_{51}N_2O_5F_6PAg$	$C_{32}H_{30}N_4O_2$
Formula weight	528.67	528.67	908.18	502.60
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	P-1	$P2_1/c$
Unit cell dimensions: a (Å)	6.0100(4)	14.6596(7)	10.3191(2)	11.1220(6)
b (Å)	6.8165(5)	9.6434(4)	11.7143(3)	6.6592(3)
c (Å)	34.162(3)	9.9858(4)	18.1490(4)	35.002(2)
α (°)	90	90	93.227(1)	90
β (°)	90.981(2)	100.994(2)	100.551(1)	95.294(3)
γ (°)	90	90	91.181(1)	90
Volume ($Å^3$)	1399.3(2)	1385.8(1)	2152.29(8)	2581.4(2)
Z	2	2	2	4
Density (calculated) (Mg/m^3)	1.255	1.267	1.401	1.293
Absorption coefficient (mm^{-1})	0.077	0.078	0.574	0.082
F(000)	564	564	937	1064
Crystal size (mm^3)	0.48 x 0.45 x 0.04	0.55 x 0.50 x 0.05	0.60 x 0.35 x 0.19	0.35 x 0.18 x 0.01
Theta range for data collection (°)	1.19 to 25.05	2.83 to 25.05	2.01 to 25.05	3.11 to 25.05
Reflections collected	8856	12283	28523	32280
Independent reflections [R(int)]	2461 [0.0358]	2453 [0.0260]	7577 [0.0306]	4565 [0.1694]
Completeness to theta (°/%)	25.05 / 99.6	25.05 / 99.9	25.05 / 99.5	25.05 / 99.9
Data / restraints / parameters	2461 / 0 / 181	2453 / 0 / 181	7577 / 0 / 535	4565 / 0 / 343
Goodness-of-fit on F^2	1.042	1.075	1.034	0.803
Final R_1 [I>2sigma(I)]	0.0468	0.0320	0.0538	0.0479
wR_2 (all data)	0.1048	0.0816	0.1555	0.0900
Largest diff. peak and hole ($e.Å^{-3}$)	0.212 and -0.169	0.268 and -0.167	1.132 and -0.764	0.214 and -0.232

Table A15. Crystal data and structure refinement for 5.24, 5.25, 5.31 and 5.32.

Compound	**5.24**	**5.25**	**5.31**	**5.32**
Empirical formula	$C_{42}H_{36}N_2O_2$	$C_{40}H_{34}N_4O_2$	$C_{73}H_{78}N_8O_{16}Cl_2Cu$	$C_{32}H_{30}N_4O_2F_6PAg$
Formula weight	600.73	602.71	1457.87	755.44
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P-1	$P2_1/m$
Unit cell dimensions: a (Å)	10.1259(4)	7.8984(6)	9.3210(6)	8.2358(6)
b (Å)	10.6707(5)	9.6948(7)	14.5689(10)	28.210(2)
c (Å)	15.5700(7)	11.3986(9)	14.9940(12)	11.0927(9)
α (°)	70.765(3)	93.225(3)	74.502(5)	90
β (°)	85.062(3)	104.846(3)	78.968(5)	100.808(5)
γ (°)	81.225(3)	110.457(3)	72.149(4)	90
Volume ($Å^3$)	1568.7(1)	780.17(10)	1854.3(2)	2531.5(3)
Z	2	1	1	2
Density (calculated) (Mg/m^3)	1.272	1.283	1.306	0.991
Absorption coefficient (mm^{-1})	0.078	0.080	0.437	0.475
F(000)	636	318	763	764
Crystal size (mm^3)	0.80 x 0.30 x 0.09	0.70 x 0.45 x 0.08	0.50 x 0.15 x 0.03	0.34 x 0.18 x 0.02
Theta range for data collection (°)	2.04 to 25.05	2.27 to 25.05	1.42 to 25.05	1.44 to 25.05
Reflections collected	20217	4733	21914	18148
Independent reflections [R(int)]	5473 [0.0542]	2723 [0.0135]	6395 [0.0711]	4560 [0.0696]
Completeness to theta (°/%)	25.05 / 98.6	25.05 / 98.1	25.05 / 97.6	25.05 / 99.8
Data / restraints / parameters	5473 / 0 / 415	2723 / 0 / 241	6395 / 0 / 517	4560 / 0 / 319
Goodness-of-fit on F^2	0.933	1.009	1.062	1.152
Final R_1 [I>2sigma(I)]	0.0413	0.0573	0.0989	0.1021
wR_2 (all data)	0.0897	0.1449	0.2768	0.2595
Largest diff. peak and hole ($e.Å^{-3}$)	0.209 and -0.192	0.564 and -0.254	1.117 and -0.817	1.569 and -3.248

Table A16. Crystal data and structure refinement for 5.34, 5.35, 5.36 and 5.41.

Compound	**5.34**	**5.35**	**5.36**	**5.41**
Empirical formula	$C_{43}H_{40}N_2O_3Cl_2Cu$	$C_{44}H_{38}N_2O_6Cl_7Ag$	$C_{44}H_{38}N_2O_4Cl_6F_2PAg$	$C_{37}H_{37}N_2O_2Cl_3F_6PAg$
Formula weight	767.21	1046.78	1048.30	900.88
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions: a (Å)	16.1118(5)	15.1083(5)	15.1421(5)	19.5439(7)
b (Å)	10.3902(3)	15.4499(4)	15.5466(5)	10.8887(4)
c (Å)	23.4499(7)	18.8077(5)	18.9122(6)	18.0618(6)
α (°)	90	90	90	90
β (°)	109.735(2)	91.017(1)	91.628(2)	102.458(2)
γ (°)	90	90	90	90
Volume ($Å^3$)	3695.1(2)	4389.4(2)	4450.3(2)	3753.2(2)
Z	4	4	4	4
Density (calculated) (Mg/m^3)	1.379	1.584	1.565	1.594
Absorption coefficient (mm^{-1})	0.779	0.936	0.902	0.860
F(000)	1596	2120	2120	1824
Crystal size (mm^3)	0.35 x 0.30 x 0.02	0.35 x 0.24 x 0.04	0.61 x 0.55 x 0.05	0.45 x 0.35 x 0.02
Theta range for data collection (°)	1.34 to 25.05	2.16 to 25.05	3.21 to 25.05	2.20 to 25.05
Reflections collected	43676	111015	44993	45840
Independent reflections [R(int)]	6539 [0.0639]	7751 [0.0399]	7859 [0.0390]	6625 [0.0698]
Completeness to theta (°/%)	25.05 / 100.0	25.05 / 99.9	25.05 / 99.7	25.05 / 99.9
Data / restraints / parameters	6539 / 0 / 480	7751 / 0 / 541	7859 / 0 / 560	6625 / 0 / 490
Goodness-of-fit on F^2	1.072	1.045	1.022	1.060
Final R_1 [I>2sigma(I)]	0.0443	0.0229	0.0257	0.0462
wR_2 (all data)	0.1177	0.0572	0.0647	0.1272
Largest diff. peak and hole ($e.Å^{-3}$)	0.716 and -0.578	0.651 and -0.660	0.695 and -0.745	0.810 and -0.711

Table A17. Crystal data and structure refinement for 5.42, 5.43, 5.44 and 5.45.

Compound	**5.42**	**5.43**	**5.44**	**5.45**
Empirical formula	$C_{37}H_{37}N_2O_6Cl_4Ag$	$C_{38}H_{37}N_2O_5Cl_3F_3SAg$	$C_{36}H_{36}N_2O_2Br_2Zn$	$C_{37}H_{40}N_3O_6Cu$
Formula weight	855.36	904.98	753.86	654.49
Temperature (K)	93(2)	93(2)	93(2)	93(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	Pbca	$P2_1/n$
Unit cell dimensions: a (Å)	19.1695(9)	19.8315(7)	8.4893(2)	8.8229(8)
b (Å)	10.8412(5)	11.1779(4)	19.4525(5)	37.128(4)
c (Å)	18.1478(7)	17.8907(6)	40.3735(11)	9.8621(9)
α (°)	90	90	90	90
β (°)	102.531(3)	101.272(2)	90	91.496(4)
γ (°)	90	90	90	90
Volume ($Å^3$)	3681.6(3)	3889.4(2)	6667.2(3)	3229.5(5)
Z	4	4	8	4
Density (calculated) (Mg/m^3)	1.543	1.545	1.502	1.346
Absorption coefficient (mm^{-1})	0.886	0.837	3.168	0.408
F(000)	1744	1840	3056	1382
Crystal size (mm^3)	0.30 x 0.10 x 0.01	0.35 x 0.30 x 0.02	0.35 x 0.15 x 0.03	0.70 x 0.20 x 0.02
Theta range for data collection (°)	2.30 to 25.05	2.16 to 25.05	2.09 to 25.05	2.34 to 25.05
Reflections collected	40366	41341	94012	19287
Independent reflections [R(int)]	6469 [0.1155]	6893 [0.0734]	5895 [0.1344]	5617 [0.0631]
Completeness to theta (°/%)	25.05 / 99.4	25.05 / 99.9	25.05 / 100.0	25.05 / 98.1
Data / restraints / parameters	6469 / 0 / 474	6893 / 0 / 488	5895 / 0 / 388	5617 / 0 / 422
Goodness-of-fit on F^2	0.936	1.040	1.153	1.035
Final R_1 [I>2sigma(I)]	0.0566	0.0825	0.0983	0.0571
wR_2 (all data)	0.1439	0.2225	0.2837	0.1386
Largest diff. peak and hole ($e.Å^{-3}$)	1.065 and -0.886	1.371 and -0.943	2.793 and -1.450	0.735 and -0.566

Table A18. Crystal data and structure refinement for 5.46 and 5.47.

Compound	**5.46**	**5.47**
Empirical formula	$C_{36.50}H_{37}N_2O_2Br_2ClZn$	$C_{36}H_{36}N_2O_2Cl_2Zn$
Formula weight	796.32	664.94
Temperature (K)	93(2)	93(2)
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2/n
Unit cell dimensions: a (Å)	12.9431(5)	14.6252(9)
b (Å)	14.8867(6)	12.9069(7)
c (Å)	17.9428(8)	35.878(2)
α (°)	92.203(3)	90
β (°)	91.433(2)	92.825(2)
γ (°)	91.184(2)	90
Volume ($Å^3$)	3452.8(2)	6764.3(7)
Z	4	8
Density (calculated) (Mg/m^3)	1.532	1.306
Absorption coefficient (mm^{-1})	3.138	0.917
F(000)	1612	2768
Crystal size (mm^3)	0.30 x 0.25 x 0.01	0.60 x 0.39 x 0.01
Theta range for data collection (°)	2.35 to 25.05	1.14 to 25.05
Reflections collected	39172	45990
Independent reflections [R(int)]	12004 [0.1255]	12001 [0.0947]
Completeness to theta (°/%)	25.05 / 98.1	25.05 / 100.0
Data / restraints / parameters	12004 / 0 / 802	12001 / 0 / 803
Goodness-of-fit on F^2	0.751	1.015
Final R_1 [I>2sigma(I)]	0.0506	0.1153
wR_2 (all data)	0.0919	0.2934
Largest diff. peak and hole ($e.Å^{-3}$)	0.742 and -0.569	2.040 and -2.033

Appendix 2: Publication

Listed below is the publication that has resulted so far from the research work described in this thesis.

Justine R. A. Cottam and Peter J. Steel, Synthesis of a family of heterocyclic ligands derived from bisphenols: new flexible bridging ligands for use in metallosupramolecular chemistry, *Tetrahedron*, **2008**, *64*, 2915-2923.

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